Convenient Preparation of N-Monosubstituted *S*,*S*-Diarylsulfodiimides Using Fluoro-λ^6-sulfanenitriles

Toshiaki Yoshimura,* Hiroki Ishikawa, Tetsuo Fujie, Eiichi Takata, Ryuta Miyatake, Hiroshi Kita, Eiichi Tsukurimichi

Department of Applied Chemistry, Graduate School of Science and Engineering, University of Toyama, Gofuku, Toyama 930-8555, Japan
Fax +81(76)4456850; E-mail: yosimura@eng.u-toyama.ac.jp

Received 11 January 2008; revised 29 February 2008

Abstract: The reaction of fluorodiphenyl-λ^6-sulfanenitrile with primary alkyl- or aryl-amines in the presence of acid catalysts or tertiary amines gave N-monosubstituted *S*,*S*-diphenylsulfodiimides effectively.

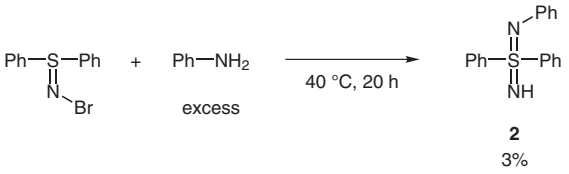
Key words: fluorodiphenyl-λ^6-sulfanenitrile, acid catalyst, N-monosubstituted *S*,*S*-diphenylsulfodiimides

The chemistry of sulfodiimides[1] is interesting from the point of view that they have structures which are isoelectronic with sulfones, are very stable and react through the two basic functionalities in the molecule. Such compounds can be expected to have characteristic reactions and applications. Recently we reported a synthetic application of N-monosubstituted *S*,*S*-diphenylsulfodiimides in N-sulfenylation, which afforded the corresponding *N*-sulfenylsulfodiimides. These compounds, upon moderate thermolysis, generated sulfenylnitrenes, which could be trapped with olefins to give *N*-sulfenylazyridines stereospecifically in high yields.[2]

Though there are some reports on the synthesis of *S*,*S*-dialkylsulfodiimides,[3] only a few *S*,*S*-diarylsulfodiimides have been prepared. Furukawa et al.[4] prepared *N*-*p*-tosyl-*S*,*S*-diarylsulfodiimides by the reaction of N-unsubstituted *S*,*S*-diarylsulfimides with chloramine-T. However, direct N-monoalkylation of sulfodiimides is very difficult to control and the only example of *N*-monoalkyl-*S*,*S*-diarylsulfodiimides came from the reaction of *N*-halo-*S*,*S*-diarylsulfimides with primary alkylamines.[5] However, this method is not suitable for the synthesis of *N*-monoarylsulfodiimides. Recently, we have prepared an unusual type of compound, λ^6-sulfanenitriles, bearing a sulfur–nitrogen triple bond, and have investigated their reactivity.[6] Our discovery of fluoro-λ^6-sulfanenitriles[7] inspired us to prepare N-monosubstituted *S*,*S*-diarylsulfodiimides. Previously we reported that the reaction of fluorodiphenyl-λ^6-sulfanenitrile with primary amines gave the corresponding N-monosubstituted sulfodiimides, including *N*-arylsulfodiimides.[7a] In this paper, we report the preparation of a further variety of N-monosubstituted sulfodiimides. Furthermore, we report an improvement of the yields through the use of acid catalysts and base.

The reactions of fluorodiphenyl-λ^6-sulfanenitrile (**1**) with three equivalents of either butylamine or aniline, were carried out under the various conditions shown in Table 1. The reaction with butylamine in acetonitrile gave the corresponding *N*-butyl-*S*,*S*-diphenylsulfodiimide in only 12% yield, with the remainder of the reaction mixture consisting of unreacted λ^6-sulfanenitrile (Table 1, entry 1). Interestingly, since *N*-arylsulfodiimides are difficult to prepare by other methods, the reaction with aniline under the same reaction conditions gave *N*-arylsulfodiimides in 62% yield (entry 13). Attempts to synthesize *N*-phenyl-*S*,*S*-diphenylsulfodiimide by Furukawa's method[5] using *N*-bromo-*S*,*S*-diphenylsulfimide and aniline without solvent gave the desired product in only 3% yield (Scheme 1).

Since no X-ray crystal structures are available for diarylsulfodiimides, the structure of the *N*-phenylsulfodiimide was also confirmed by X-ray crystallographic analysis. An ORTEP drawing and some selected bond lengths and angles are listed in Figure 1. The S–N bond lengths are



Scheme 1

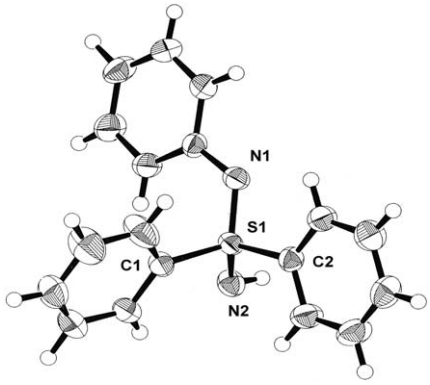
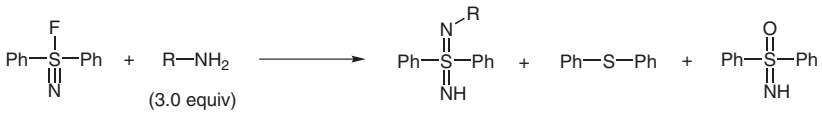


Figure 1 The molecular structure of *N*-phenyl-*S*,*S*-diphenylsulfodiimide. Selected bond lengths (Å) and bond angles (°): S(1)–N(1), 1.546(1); S(1)–N(2), 1.526(2); S(1)–C(1), 1.798(2); S(1)–C(2), 1.788(2); N(1)–S(1)–N(2), 126.02(9); C(1)–S(1)–C(2), 104.10(8); N(1)–S(1)–C(1), 99.71(8); N(1)–S(1)–C(2), 110.46(8); N(2)–S(1)–C(1), 112.91(9); N(2)–S(1)–C(2), 102.01(9).

SYNTHESIS 2008, No. 12, pp 1835–1840
Advanced online publication: 16.05.2008
DOI: 10.1055/s-2008-1067090; Art ID: F00108SS

Table 1 Reaction of Fluorodiphenyl-λ^6-sulfanenitrile (**1**) with Butylamine or Aniline



Entry	R	Conditions				Yield (%)[a]			
		Solvent	Temp (°C)	Catalyst (1.2 equiv)	Time (h)	**2**	**3**	**4**	Recovered
1	*n*-Bu	MeCN	30	–	16	12	0	0	85
2	*n*-Bu	MeCN	30	AcOH	16	51	–	–	–
3	*n*-Bu	MeCN	30	TFA	8	90	–	–	–
4	*n*-Bu	none	30	–	8	20	0	1	76
5	*n*-Bu	none	30	AcOH	8	73	0	24	0
6	*n*-Bu	none	30	TFA	4	98	0	0	0
7	*n*-Bu	none	30	Et_3N	8	18	0	3	76
8	*n*-Bu	none	30	Et_3N	24	59	0	6	32
9	*n*-Bu	none	30	DABCO	8	46	0	4	40
10	*n*-Bu	none	30	DABCO	24	87	0	4	0
11	*n*-Bu	none	30	pyridine	8	14	0	5	72
12	*n*-Bu	none	30	pyridine	24	38	0	5	51
13	Ph	MeCN	30	–	16	62	11	2	0
14	Ph	MeCN	50	–	16	50	22	2	0
15	Ph	MeCN	30	AcOH	16	64	8	–	–
16	Ph	MeCN	30	TFA	8	49	15	–	–
17	Ph	none	30	–	1	92	5	2	0
18	Ph	none	30	–	20	90	7	2	0
19	Ph	none	30	AcOH	0.5	86	6	6	0
20	Ph	none	30	AcOH	8	62	12	–	–
21	Ph	none	30	TFA	0.5	85	11	0	0
22	Ph	none	30	TFA	4	29	41	–	–
23	Ph	none	30	Et_3N	8	13	0	5	80
24	Ph	none	30	DABCO	8	84	0	8	2
25	Ph	none	30	pyridine	1	98	0	0	0

[a] Determined by ^1H NMR analysis.

very similar to those found in of *S*,*S*-dimethylsulfodiimide (1.536 Å).[8,9]

In the case of the reaction in acetonitrile, the yield of *N*-phenylsulfodiimide formation was better than that of the *N*-butylsulfodiimide, however, the reaction of aniline gave the by-product diphenyl sulfide (**3**; entry 13). Conducting the reaction at 50 °C reduced the yield of the *N*-phenylsulfodiimide and gave rise to increased formation of sulfide **3** (entry 14). Subsequent reactions were, therefore, all carried out at 30 °C.

Addition of acids such as acetic (AcOH) or trifluoroacetic (TFA) acid greatly accelerated the formation of the *N*-butylsulfodiimide, the effect of the latter being larger than that of the former (entries 2 and 3). The acceleration caused by TFA in the reaction with butylamine is clearly demonstrated in Figure 2. In the case of an aromatic

amine, although the reaction was also accelerated by acid, the use of the strong acid TFA reduced the yield of the *N*-phenylsulfodiimide compared to the use of AcOH, and increased the amount of by-product (PhSPh) and tar (entries 15 and 16).

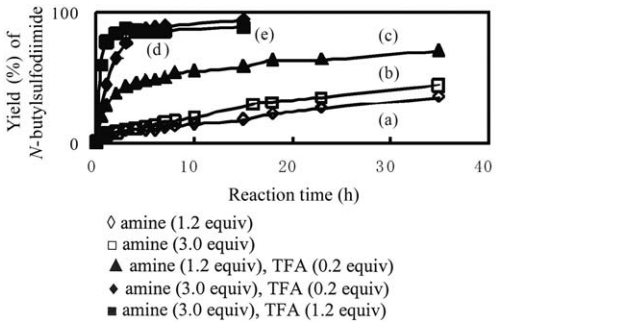
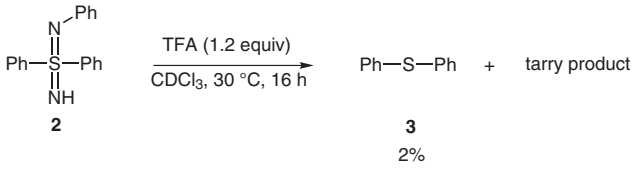


Figure 2 Time dependence of yields (%) of *N*-butylsulfodiimide in the reaction of fluorodiphenyl-λ^6-sulfanenitrile (**1**) with butylamine at 30 °C in MeCN.

In order to examine the possibility that the use of acid causes the decomposition of the product *N*-phenylsulfodiimide, the decomposition of **2** in an NMR tube at 30 °C was followed for 16 hours. The formation of PhSPh (2% yield), together with an unidentified tarry product (Scheme 2) suggested that decomposition of the *N*-phenylsulfodiimide was indeed catalyzed by an acid, though the reaction conditions were not same. The formed product **2** also decomposed in the presence of TFA when the reaction in Table 1, entry 21 was continued for longer times (Table 1, entry 22).



Scheme 2

The reaction was greatly improved when performed without solvent. The time required for the aliphatic amine to react in the absence of solvent was found to be reduced compared to that in acetonitrile; addition of acid further improved the results compared to the reaction in acetonitrile (entries 4–6). These results may be an effect of concentration. In the case of an aromatic amine, when the reaction was performed without solvent an exothermic reaction occurred and the rate of the reaction significantly increased; the reaction was almost complete in one hour, even without addition of acid (entry 17). Longer reaction times (20 h) afforded only a small increase in the amount of decomposition products (entry 18). Addition of acid resulted in faster reaction times (<30 min), but also increased the formation of PhSPh; prolonged reaction times gave large amounts of decomposition products (entries 19–22). However, even in the absence of acid, the reaction can be considered to be catalyzed by HF formed in the reaction as a form of conjugate acid of the amine. Addition of triethylamine (1.2 equiv) to the reaction with aniline, retarded the reaction and gave only 13% of the sulfodiimide and 80% recovered starting material after 8 hours (entry 23). This result provides evidence for the catalytic role of HF. The acid catalysts are thus actually the conjugate acid of the strongest basic amines in the system. There are two possible catalytic mechanisms. One involves protonation of the thiazyl nitrogen atom and the other involves general acid catalysis to assist removal of the fluoride anion. Loss of a fluoride anion is known to be catalyzed by acid in the hydrolysis of acetyl fluoride in aqueous solution.[10] Furthermore, we have previously reported that the fluoro-λ^6-sulfanenitrile (**1**) undergoes hydrolysis in aqueous solvent through a dissociative mechanism catalyzed by acid.[11] The reaction of **1** with aniline, without the addition of acid, is considered to be catalyzed by aniline hydrofluoride as shown in Figure 3, however, in the presence of triethylamine, its hydrofluoride is formed instead of aniline hydrofluoride. Since the acidity of the conjugate acid of triethylamine is weaker than that of aniline and thus the catalytic activity is smaller, the rate of the reaction is retarded. The acid catalysts are also effective in the reaction with aromatic amines, however, acid-catalyzed decomposition of *N*-arylsulfodiimides to give diphenyl sulfide and a tarry product, limited the product yields. The results suggest that the HF generated effectively catalyzes this reaction to afford *N*-arylsulfodiimides in moderate yields.[10,11]

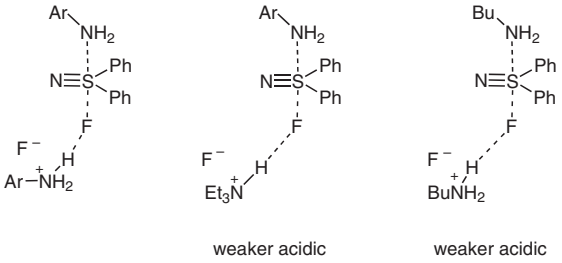


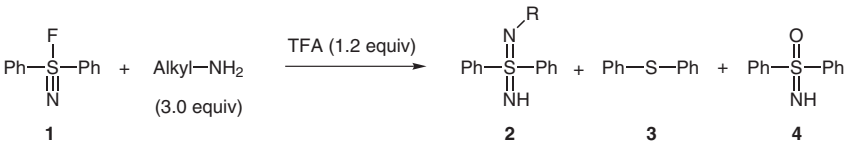
Figure 3 Catalytic action of the conjugate acids of amines

In spite of the stronger nucleophilicity of the alkylamine compared to the aromatic amine, the reaction with butylamine was slower than that with aniline. This result may be explained by the weaker catalytic effect of conjugate acid (hydrofluoride) from the more basic butylamine than that of the aromatic amine as shown in Figure 3. When both butylamine and aniline were mixed in the same reaction system, without solvent, at 30 °C for 24 hours the *N*-butylsulfodiimide was afforded in 36% yield; only 3% of the *N*-phenylsulfodiimide together with 5% of **4** and 50% starting materials were recovered, suggesting that the weaker nucleophilic aniline reacts slower than the stronger butylamine under the same weaker catalytic conditions. Although the reaction was slow in the presence of triethylamine, the interesting result that HF was trapped by the more basic amine, thus inhibiting the formation of diphenyl sulfide and tarry product, lead us to investigate the use of various tertiary amines as shown in entries 7–12

and 23–25. Though none of the *tert*-amines studied significantly affected the rate of reaction with butylamine (entries 7–12), alkyl *tert*-amines slowed down the rate of formation of *N*-phenylsulfodiimide (entries 23 and 24) and all *tert*-amines were found to inhibit the formation of the sulfide **3**. The use of pyridine was found to give the maximum yield of the *N*-phenylsulfodiimide, whilst not retarding the rate of the reaction (entry 25). Therefore, the best conditions for the reaction with aromatic amines involves the use of pyridine, while those for the reaction with aliphatic amines are to use TFA without solvent. The reaction of **1** with various aliphatic amines in the presence of TFA (1.2 equiv) are shown in Table 2 and the reaction with various aromatic amines in the presence of pyridine (1.2 equiv) without using solvent are shown in Table 3. In the case of gaseous amines, the amines were once condensed at low temperature and the reactions were carried out from –80 °C to room temperature under normal pressure. The formation of the sulfoximides **4** reduced the yield of the desired sulfodiimides **2** (Table 2). In the presence of pyridine, the rate of the reactions were found to be slower with some *ortho*-substituted anilines, in these cases, the reaction time was extended to three hours, to give the corresponding *N*-arylsulfodiimides in very good yields. The reaction with other substituted anilines seems to be accelerated by the addition of pyridine, to give the sulfodiimides in very good yields. None of the reactions in the presence of pyridine gave the decomposition product, PhSPh.

In summary, N-monosubstituted *S*,*S*-diphenylsulfodiimides have been conveniently prepared in high yields by the

Table 2 Reaction of **1** with Aliphatic Amines in the Presence of TFA without Solvent

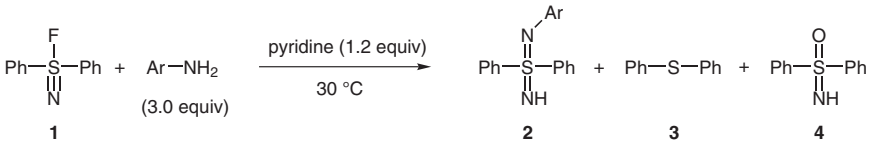


1 2 3 4

Amine	Conditions		Yield (%)[a]			
R	Temp (°C)	Time (h)	**2**	**3**	**4**	Recovered
H[b]	–80 to r.t.	8	74	0	22	0
Me[b]	–80 to –40	4	79	0	17	0
n-Pr	30	4	96	0	0	0
n-Bu	30	4	98	0	0	0
t-Bu	30	4	no reaction			

[a] Determined by ^{1}H NMR analysis.
[b] Due to the difficulty of measuring exact amounts of gaseous amines, an excess of amine was used.

Table 3 Reaction of **1** with Aromatic Amines in the Presence of Pyridine without Solvent at 30 °C



1 2 3 4

Amine	Time (h)	Yield (%)[a]			
Ar		**2**	**3**	**4**	Recovered
o-MeC_6H_4	1	38	0	2	57
	3	94	0	4	0
p-MeC_6H_4	1	96	0	1	0
o-MeC_6H_4	1	93	0	5	0
p-MeC_6H_4	1	92	0	1	5
o-ClC_6H_4	1	57	0	5	37
	3	93	0	6	0
m-ClC_6H_4	1	96	0	2	0
p-ClC_6H_4	1	97	0	2	0

[a] Determined by ^{1}H NMR analysis.

reaction of fluorodiphenyl-λ^6-sulfanenitriles (**1**) with various primary amines. The reaction was found to be catalyzed either by HF generated in the reaction, or by additional acids such as trifluoroacetic acid or acetic acid. *N*-Alkylsulfodiimides were best prepared under solvent-free conditions in the presence of small amounts of TFA, while *N*-arylsulfodiimides were optimally prepared under solvent-free conditions in the presence of small amount of pyridine. Use of organic solvent was found to reduce the yield of N-substituted sulfodiimides.

All reagents and solvents were obtained commercially and were purified by general methods when necessary. Analytical TLC was performed on Merck plastic sheets coated in Silica gel 60 F_{254}. Merck silica gel (60) was used for column chromatography. Infrared spectra (IR) were recorded on a Horiba FT-710 spectrometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained on a JEOL-JNM-A400 NMR spectrometer in $CDCl_3$ with TMS as an internal standard. Chemical shifts (δ) are measured in ppm and coupling constants (*J*) are in hertz (Hz). Mass spectra (MS) were recorded on a JEOL-JMS-D300 mass spectrometer. Melting point were measured on a Yanaco Mp-j3 melting point apparatus. Elemental analysis were performed on a Yanaco MT-5 CHN CORDER.

Preparation of *N*-Alkyl- and *N*-Aryl-*S*,*S*-diphenylsulfodiimides 2; Typical Procedure

To fluorodiphenyl-λ^6-sulfanenitrile (**1**; 1.00 g, 4.57 mmol) was added a solution of TFA (0.42 mL, 5.48 mmol, 1.2 equiv) in butylamine (1.37 mL, 13.8 mmol, 3.0 equiv) and the mixture was allowed to react at 30 °C whilst monitoring by TLC ($CHCl_3$–MeOH, 20:1). The solution was diluted with $CHCl_3$ (50 mL), washed with dilute HCl (3%, 20 × 5 mL) and extracted with $CHCl_3$ (20 × 2 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and the filtrate was evaporated. The residue was purified by silica gel column chromatography ($CHCl_3$–MeOH, 8:1) to give the crude *N*-butyl-*S*,*S*-diphenylsulfodiimide, which was further recrystallized from MeOH (82% yield, 1.02 g, 3.74 mmol).

***S*,*S*-Diphenylsulfodiimide**

Colorless crystals; mp 88–90 °C (C_6H_6) (Lit.[5] 91.0–92.0 °C).

IR (KBr): 3155, 3067, 1446, 1130, 1092, 1024, 928 cm^{-1} (Lit.[5] 3160, 1130, 1090, 1065, 930 cm^{-1}).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.32 (br, 1 H), 7.27–7.47 (m, 6 H), 8.13–8.16 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 127.3, 128.9, 131.8, 145.2.

***N*-Methyl-*S*,*S*-diphenylsulfodiimide**

Colorless crystals; mp 115–117 °C (C_6H_6).

IR (KBr): 3149, 3059, 2960, 1444, 1180, 1092, 1022, 993 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.81 (s, 3 H), 7.43–7.47 (m, 6 H), 8.06–8.09 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.1, 127.9, 128.9, 131.7, 142.5.

Anal. Calcd for $C_{13}H_{14}N_2S$: C, 67.79; H, 6.13; N, 12.16. Found: C, 68.13; H, 6.22; N, 12.16.

***N*-Propyl-*S*,*S*-diphenylsulfodiimide**

Colorless crystals; mp 118–119 °C (C_6H_6–hexane) (Lit.[5] 117.5–118.5 °C).

IR (KBr): 3155, 2950, 1445, 1168, 1121, 1082, 1019 cm^{-1} (Lit.[5] 3160, 1170, 1110, 1035, 1010 cm^{-1}).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (t, *J* = 7.2 Hz, 3 H), 1.54 (sext, *J* = 7.2 Hz, 2 H), 3.01 (t, *J* = 7.2 Hz, 2 H), 7.41–7.46 (m, 6 H), 8.01–8.11 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.0, 26.3, 44.9, 128.0, 128.9, 131.5, 143.3.

Anal. Calcd for $C_{15}H_{18}N_2S$: C, 69.73; H, 7.02; N, 10.84. Found: C, 70.06; H, 6.98; N, 10.74.

***N*-Butyl-*S*,*S*-diphenylsulfodiimide**

Colorless crystals; mp 93–94 °C (C_6H_6–hexane) (Lit.[5] 97.5–98.0 °C).

IR (KBr): 3150, 2930, 1442, 1180, 1082, 1020, 982 cm^{-1} (Lit.[5] 3160, 1180, 1085, 1060, 1025, 985 cm^{-1}).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (s, 3 H), 1.42 (sext, *J* = 7.2 Hz, 2 H), 1.63 (quint, *J* = 7.2 Hz, 2 H), 3.04 (t, *J* = 7.2 Hz, 2 H), 7.41–7.47 (m, 6 H), 8.08–8.10 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.4, 20.5, 35.3, 42.8, 128.0, 128.8, 131.5, 143.2.

Anal. Calcd for $C_{16}H_{20}N_2S$: C, 70.54; H, 7.40; N, 10.28. Found: C, 70.68; H, 7.31; N, 10.16.

***N*-Phenyl-*S*,*S*-diphenylsulfodiimide**

Colorless crystals; mp 154 °C (MeOH).

IR (KBr): 3170, 1598, 1485, 1441, 1287, 1260, 1081, 959 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.83–6.88 (m, 1 H), 7.11–7.12 (m, 4 H), 7.43–7.50 (m, 6 H), 8.16–8.21 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.8, 123.3, 128.8, 129.1, 132.0, 143.1, 145.7.

Anal. Calcd for $C_{18}H_{16}N_2S$: C, 73.94; H, 5.52; N, 9.58. Found: C, 74.11; H, 5.65; N, 9.26.

X-ray crystal data; Empirical formula: $C_{18}H_{16}N_2S$; Formula weight 292.40; Crystal system = triclinic; Space group P1 (#2); Unit cell dimensions: *a* = 6.446(1) Å, *b* = 10.772(2) Å, *c* = 12.241(2) Å; α = 106.21(1)°, β = 101.64(2)°, γ = 105.67(2)°; *V* = 749.8(2) Å^3; T = 296 K; *Z* = 2; μ(Mo Kα) = 2.10 cm^{-1}; 4573 reflections measured, 3156 unique (R_{int} = 0.043); final *R* value 0.060. Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 679450.

***N*-*o*-Tolyl-*S*,*S*-diphenylsulfodiimide**

Colorless crystals; mp 119 °C (MeOH).

IR (KBr): 3185, 1596, 1480, 1254, 1180, 1075, 950 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.50 (s, 3 H), 6.75–6.79 (td, *J* = 7.2, 1.2 Hz, 2 H), 6.86–6.90 (td, *J* = 7.2, 1.2 Hz, 2 H), 7.13–7.16 (m, 2 H), 7.42–7.49 (m, 6 H), 8.19–8.23 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.0, 120.5, 120.7, 126.0, 128.0, 129.1, 130.2, 131.9, 132.8, 143.5, 144.0.

Anal. Calcd for $C_{19}H_{18}N_2S$: C, 74.47; H, 5.92; N, 9.14. Found: C, 74.49; H, 6.00; N, 8.95.

***N*-*p*-Tolyl-*S*,*S*-diphenylsulfodiimide**

Colorless crystals; mp 124 °C (MeOH).

IR (KBr): 3210, 3040, 1610, 1505, 1475, 1445, 1280, 1255, 1180, 1140, 950, 820 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.22 (s, 3 H), 6.94 (d, *J* = 7.6 Hz, 2 H), 7.05 (d, *J* = 7.6 Hz, 2 H), 7.44–7.48 (m, 6 H), 8.17–8.19 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.6, 123.2, 128.0, 129.1, 129.4, 130.1, 131.9, 142.9, 143.2.

Anal. Calcd for $C_{19}H_{18}N_2S$: C, 74.47; H, 5.92; N, 9.14. Found: C, 74.51; H, 5.88; N, 9.15.

***N*-*o*-Methoxyphenyl-*S*,*S*-diphenylsulfodiimide**
Colorless crystals; mp 111 °C (MeOH).

IR (KBr): 3278, 3056, 3000, 1500, 1492, 1444, 1255, 1232, 1084, 1045, 1028, 949 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.35 (br, 1 H), 3.83 (s, 3 H), 6.68–6.72 (m, 1 H), 6.83–6.88 (m, 2 H), 7.13–7.15 (dd, *J* = 6.8, 1.2 Hz, 1 H), 7.42–7.48 (m, 6 H), 8.19–8.23 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.7, 111.5, 120.7, 121.7, 123.7, 128.0, 129.0, 131.8, 134.6, 143.5, 153.8.

Anal. Calcd for $C_{19}H_{18}N_2OS$: C, 70.78; H, 5.63; N, 8.69. Found: C, 70.59; H, 5.83; N, 8.39.

***N*-*p*-Methoxyphenyl-*S*,*S*-diphenylsulfodiimide**
Colorless crystals; mp 111 °C (MeOH).

IR (KBr): 3225, 3050, 3000, 1500, 1470, 1440, 1255, 1230, 1080, 1030, 950 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.72 (s, 3 H), 6.85 (td, *J* = 8.8, 2.4 Hz, 2 H), 7.08 (td, *J* = 8.8, 2.4 Hz, 2 H), 7.43–7.48 (m, 6 H), 8.18 (dd, *J* = 8.8, 2.4 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4, 114.3, 124.4, 128.1, 129.1, 131.9, 138.6, 143.1, 154.2.

MS: *m*/*z* = 292 [M^+].

Anal. Calcd for $C_{19}H_{18}N_2OS$: C, 70.78; H, 5.63; N, 8.69. Found: C, 70.59; H, 5.71; N, 8.60.

***N*-*o*-Chlorophenyl-*S*,*S*-diphenylsulfodiimide**
Colorless crystals; mp 144 °C (MeOH).

IR (KBr): 3199, 3056, 1581, 1469, 1309, 1286, 1248, 1153, 1128, 1082, 1060, 958 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.77 (td, *J* = 7.6, 1.6 Hz, 1 H), 6.92 (td, *J* = 7.6, 1.6 Hz, 1 H), 7.32 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.36 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.43–7.50 (m, 6 H), 8.21–8.26 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 121.4, 122.5, 126.9, 128.2, 129.16, 129.20, 129.8, 132.2, 142.7, 142.8.

Anal. Calcd for $C_{18}H_{15}N_2ClS$: C, 66.15; H, 4.63; N, 8.57. Found: C, 66.13; H, 4.68; N, 8.47.

***N*-*m*-Chlorophenyl-*S*,*S*-diphenylsulfodiimide**
Colorless crystals; mp 139 °C (MeOH).

IR (KBr): 3155, 1585, 1485, 1470, 1360, 1259, 970 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.82 (td, *J* = 7.2, 1.6 Hz, 1 H), 7.00–7.06 (m, 2 H), 7.19 (s, 1 H), 7.43–7.52 (m, 6 H), 8.13–8.20 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.7, 121.1, 123.4, 127.9, 129.2, 129.6, 132.2, 134.2, 142.6, 147.3.

Anal. Calcd for $C_{18}H_{15}N_2ClS$: C, 66.15; H, 4.63; N, 8.57. Found: C, 66.37; H, 4.74; N, 8.42.

***N*-*p*-Chlorophenyl-*S*,*S*-diphenylsulfodiimide**
Colorless crystals; mp 154 °C (MeOH).

IR (KBr): 3150, 3040, 1585, 1480, 1440, 1280, 1250, 1180, 1140, 1080, 1020, 950 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.21 (br, 1 H), 7.06–7.11 (m, 4 H), 7.44–7.50 (m, 6 H), 8.16 (dd, *J* = 6.4, 1.2 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 124.4, 125.8, 128.0, 128.8, 129.2, 132.2, 142.7, 145.5.

MS: *m*/*z* = 328, 326 [M^+].

Anal. Calcd for $C_{18}H_{15}N_2ClS$: C, 66.15; H, 4.63; N, 8.57. Found: C, 66.26; H, 4.60; N, 8.59.

References

(1) Haake, M. *The Chemistry of S,S-Diorgano-Sulfodiimides,* In *Topics in Sulfur Chemistry*, Vol. 1; Senning, A., Ed.; Georg Thieme: Stuttgart, **1976**, Chap. 3, 185.
(2) Yoshimura, T.; Fujie, T.; Fujii, T. *Tetrahedron Lett.* **2007**, *48*, 427.
(3) (a) Appel, R.; Fehlhaber, H. W.; Hnssgen, D.; Schöllhorn, R. *Chem. Ber.* **1966**, *99*, 3108. (b) Laughlin, R. G.; Yellin, W. *J. Am. Chem. Soc.* **1967**, *89*, 2435.
(4) (a) Furukawa, N.; Akutagawa, K.; Yoshimura, T.; Akasaka, T.; Oae, S. *Synthesis* **1979**, *4*, 289. (b) Furukawa, N.; Omata, T.; Oae, S. *Chem. Commun.* **1973**, 590.
(5) Furukawa, N.; Akutagawa, K.; Oae, S. *Phosphorus Sulfur Relat. Elem.* **1984**, *20*, 1.
(6) Yoshimura, T. *Rev. Heteroat. Chem.* **2000**, *22*, 101.
(7) (a) Yoshimura, T.; Kita, H.; Takeuchi, K.; Takata, E.; Hasegawa, K.; Shimasaki, C.; Tsukurimichi, E. *Chem. Lett.* **1992**, *8*, 1433. (b) Yoshimura, T.; Ohkubo, M.; Fujii, T.; Kita, H.; Wakai, Y.; Ono, S.; Morita, H.; Shimasaki, C.; Horn, E. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1629.
(8) Webb, N. S.; Gloss, R. A. *Tetrahedron Lett.* **1967**, 1043.
(9) Prince, E. *Acta Crystallogr., Sect. B* **1975**, *31*, 2536.
(10) Bunton, C. A.; Fendler, J. H. *J. Org. Chem.* **1966**, *31*, 2307.
(11) Dong, T.; Fujii, T.; Murotani, S.; Dai, H.; Ono, S.; Morita, H.; Shimasaki, C.; Yoshimura, T. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 945.