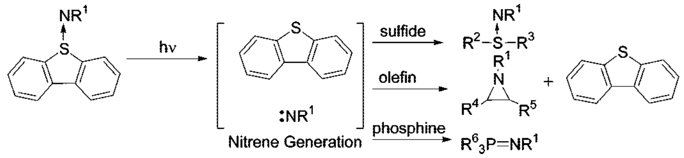
Generation of Nitrene by the Photolysis of *N*-Substituted Iminodibenzothiophene

Hiroyuki Morita,[*,†] Atsushi Tatami, Tetsuo Maeda, Byung Ju Kim, Wataru Kawashima,
Toshiaki Yoshimura,[†] Hitoshi Abe,[†] and Takeshi Akasaka[‡]

Department of Material Systems Engineering and Life Science, Faculty of Engineering, University of Toyama, 3190 Gofuku, Toyama 930-8555, Japan, and Center for Tsukuba Advanced Research Alliance (TARA Center), University of Tsukuba, Tsukuba, Ibaraki 305-8577 Japan

morita@eng.u-toyama.ac.jp

Received April 25, 2008



To evaluate the ability of dibenzothiophene *N*-substituted sulfilimines as photochemical nitrene sources, their photolyses in the presence of several trapping reagents, such as sulfides, olefins, and phosphorus compounds, were performed. In the reactions, the corresponding imino-transfer compounds, namely sulfilimines, aziridines, and iminophosphoranes, were formed in good yields, indicating dibenzothiophene *N*-tosyl and *N*-acylsulfilimines have a potent nature as nitrogen sources.

---

1. Introduction

It is reported that sulfilimines and sulfoxides decompose photochemically and afford the corresponding imino- or oxygen-transfer products in the presence of trapping reagents.[1] For example, Hayashi and Swern reported that the photolysis of *N*-benzoyliminodimethyl sulfilimine in the presence of several olefins afforded the corresponding aziridines, the photo-Curtius rearrangement product, i.e., isocyanate, and benzamide.[2] Furukawa and Oae et al. reported the photolysis of diphenyl *N*-acylsulfilimine to afford aryl isocyanate and diphenyl sulfide as major products.[3] Recently, we have revealed that photolyses of thianthrene *N*-tosylsulfilimines generate nitrene to afford the imino-transfer products in the presence of diphenyl sulfide or several olefins.[4,5]

In the case of sulfoxides, it was reported that the photolysis of dibenzothiophene oxide (**1**) afforded dibenzothiophene (**2a**) and oxidized products.[6]

In continuing studies seeking more efficient nitrene precursors under the photolyses, we were interested in the photolytic reactivity of the nitrogen analogues of dibenzothiophene oxide, i.e., dibenzothiophene sulfilimines **3**. Therefore, we prepared various *N*-substituted iminodibenzothiophenes **3a**−**d** and carried out their photolyses in the presence of sulfides, olefins, and phosphorus compounds as trapping reagents for nitrenes.[7] Toscano and Jenks recently reported the generation of benzoylnitrene by photolysis of sulfilimines.[8a] Very recently, Toscano and Jenks also reported the photochemistry of *N*-acyl and *N*-sulfonyldibenzothiophene sulfilimines. They have investigated their generation and nature by using the TRIR method and further chemical calculations.[8b] In a preliminary report, we have found that C$_{60}$ can act as a good

---

[*] Address correspondence to this author: Department of Chemical and Biochemical Engineering, Faculty of Engineering, Toyama University, 3190 Gofuku, Toyama 930-8555, Japan. Phone: +81-764-45-6851. Fax: +81-764-45-6703.

[†] University of Toyama.

[‡] University of Tsukuba.

(1) (a) For reviews on carbonyl and sulfonyl nitrenes, see: Lwowski, W. In *Nitrenes*; John Wiley & Sons, Ltd.: New York, 1970; Chapter 6, pp185−221, and Chapter 8, pp 245−303. (b) For reiviews on sulfilimines, see: Oae, S.; Furukawa, N. In *Sulfilimines and related derivertives*; ACS Monograph; American Chemical Society: Washington, DC, 1983; Chapter 1−5, pp 1−218.

(2) Hayashi, Y.; Swern, D. *J. Am. Chem. Soc.* **1973**, *95*, 5205–5210.

(3) Furukawa, N.; Fukumura, M.; Nishio, T.; Oae, S. *J. Chem. Soc., Perkin I* **1977**, 96–98.

(4) Fujita, T.; Kamiyama, H.; Osawa, Y.; Kawaguchi, H.; Bung, J, K.; Tatami, A.; Kawashima, W.; Maeda, T.; Nakanishi, A.; Morita, H. *Tetrahedron* **2007**, *63*, 7708.

(5) Fujita, T.; Maeda, T.; Bung, J. K.; Tatami, A.; Miyamoto, D.; Kawaguchi, H.; Tsuchiya, H.; Yoshida, M.; Kawashima, W.; Morita, H. Photolytic Aziridination by Thianthrene Sulfilimine Derivatives. *J. Sulfur Chem.* In press.

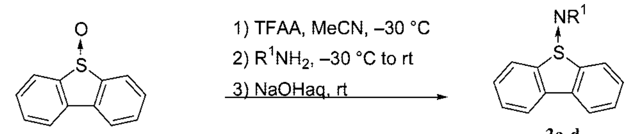
(6) Gregory, D. D.; Wan, Z.; Jenks, W. S. *J. Am. Chem. Soc.* **1997**, *119*, 94–102.

(7) Morita, H.; Tatami, A. B. J, Kim.; Yoshida, M.; Fujii, T.; Yoshimura, T. *Thermolytic and Photolytic Behavior of N-Substituted Dibenzothiophene*; 19th International Symposium on the Organic Chemistry of Sulfur, Sheffield, United Kingdom, July 2000.

(8) (a) Desikan, V.; Liu, Y.; Toscano, P. J.; Jenks, W. S. *J. Org. Chem.* **2007**, *72*, 6848–6859. (b) Desikan, V.; Liu, Y.; Toscano, P. J.; Jenks, W. S. *J. Org. Chem.* **2008**, *73*, 4398–4414.

10.1021/jo800604t CCC: $40.75

TABLE 1. Preparation of 3a–d by the Reaction of 1 with Amides in the Presence of TFAA



1 **3a-d**

entry	R^1	yield (%)^a 3
1	**3a**: R^1 = Ts	41
2	**3b**: R^1 = PhCO	76
3	**3c**: R^1 = PhCH$_2$CO	80
4	**3d**: R^1 = ^{t}BuCO	24

^{a} Isolated yield; not optimize.d.

nitrene trapping reagent upon photoirradiation of *N*-tosyldibenzothiophene sulfilimine.[9]

In this paper, we present the preparation of **3a–d** and their use for a convenient and efficient preparation of sulfilimines, aziridines, and iminophosphorane derivatives as versatile and recyclable source of nitrogen species.

2. Results and Discussion

2.1. Preparation of Iminodibenzothiohenes. *N*-Tosyliminodibenzothiophene (**3a**)[10a] was prepared by the reaction of **2a** with Chloramine T in a good yield. The compound **3a** was also prepared by the reaction of **1** with 1.5 equiv of tosylamide in the presence of 1.5 equiv of TFAA (trifluoroacetic anhydride) in acetonitrile at −30 °C following the reported procedure.[10b] Further, we carried out the reactions of **1** with several amides, such as benzamide, 2-phenylacetamide, pivalamide, and acetamide. The results are summarized in Table 1. The reaction of **1** with several amides gave the corresponding sulfilimines **3a–c**[8] in moderate to good yields (entries 1–3). However, in the reaction with pivalolyamide the yield of **3d** was low, probably due to the steric hindrance (entry 4).

The reaction sequence involves the initial formation of trifluoroacetyloxysulfonium ion (**4**)[11] and subsequent nucleophilic displacement by amide on sulfur to form the azasulfonium salt (**3a′–d′**), which yielded **3a–d** upon treatment with aq NaOH as shown in Scheme 1.

Further, we also synthesized 1-substituted *N*-tosyliminodibenzothiophene derivatives **6a**,**b** following the procedures in Scheme 2.

Imination of **2b**[12] and **2c**[13] with Chloramine T proved ineffective, and was achieved by the reaction of (*N*-tosyl)iminophenyliodinane in the presence of copper catalyst.[14]

2.2. Photolysis of 3a–d in the Presence of Several Sulfides. To estimate the ability as nitrene precursors, photolyses of **3a** were performed in the presence of diphenyl sulfide and several substituted thioanisoles, using a high-pressure mercury lamp with a Pyrex filter under Ar atmosphere. The reactions were found to give dibenzothiophene (**2a**), corresponding *N*-tosyl sulfilimine **7** or **8**, and tosylamide (**9a**), respectively. The results are summarized in Table 2. First, photolysis of **3a** in the presence of 5.0 equiv of diphenyl sulfide in several solvents was carried out to study the solvent effect (entries 1–4). It was found that diphenyl *N*-tosyl sulfilimine (**7**)[15] was obtained in the best yield in the case of 1,2-dichloroethane (DCE). Therefore, the photolyses were carried out with DCE as a solvent. In entries 4–7, the dependence of the reaction concentration was studied. However, the improvement of yield of **7** was not observed.

The photolyses of **3a** in DCE in the presence of thioanisole, 4-methyl thioanisole, 4-methoxy thioanisole, or 4-chloro thioanisole afforded the corresponding *N*-tosylsulfilimines (**8a–d**)[15] in moderate to good yields (entries 9–11).

In the previous work[4] on the photolysis of substituted thianthrene *N*-tosylsulfilimines in the presence of dipenyl sulfide, we found that the *peri*-substituents on the thianthrene benzene ring substantially increase the yield of imino-transfer product, i.e., diphenyl *N*-tosylsulfilimine, probably due to the retardation of internal recombination of nitrene initially formed. Therefore, we carried out the photolysis of 1-substituted dibenzothiophene sulfilimines **6a**,**b** under the same conditions. The results were summarized in Table 3. However, in both cases, the improvement of the yield of **7** was not observed (entries 2 and −3). Probably, it is suggested that the driving force for a good nitrene precursor in dibenzothiophene sulfilimine systems is due to the regaining of resonance energy by releasing strong electron-withdrawing imino substituents on sulfur.

2.3. Photolysis of 3a–d in the Presence of Several Olefins. Photolyses of **3a–d** in 10 equiv of several olefins for 2 h were carried out. The results are summarized in Table 4.

In the photolyses of **3a** in the presence of cyclic olefins, aziridines **10a–c**[16,17] were formed in good yields (entries 1–3). However, in the reaction of cyclohexanone (entry 5), the aziridination proceeded in a low yield,[19] apparently due to its less nucleophilic nature compared with the nature of cyclopentene, cyclohexene, and cyclooctene. In the photolyses of **3b–d** in the presence of cyclohexene, aziridines **10g–i** [20,21] were also formed in good yields (entries 6–8).

As a result, it was revealed that the photoaziridination with dibenzothiophene sulfilimines **3a–d** toward common cyclic olefins proceeded in good yields of around 60–70%, which are almost the best yields among reported results.[5]

---

(9) Nakahodo, T.; Okuda, M.; Morita, H.; Yoshimura, T.; Ishitsuka, O. M.; Tuchiya, T.; Maeda, Y.; Fujihara, H.; Akasaka, T.; Xingfa, G.; Nagase, S. *Angew. Chem., Int. Ed.* **2008**, *129*, 8–1300.

(10) (a) Svoronos, P.; Horak, V. *Synthsis* **1979**, 596–597. (b) Nakayama, J.; Otani, T.; Sugihara, Y.; Sano, Y.; Ishii, A.; Sakamoto, A. *Heteroatomchemistry* **2001**, *5*, 333–348.

(11) (a) Ashok, S. K.; Thomas, K.; Arthur, D. D.; Swern, D. *Tetrahedron Lett.* **1974**, 1503–1506. (b) Ashok, S. K.; Thomas, K.; Arthur, D. D.; Swern, D. *J. Org. Chem.* **1975**, *40*, 2758.

(12) (a) Furukawa, N.; Kimura, T.; Horie, Y.; Owaga, S.; Iwasaki, F. *Heteroatomchemistry* **1993**, *4*, 243. (b) Gilman, H.; Jacoby, L. A. *J. Org. Chem.* **1938**, *3*, 108–119. (c) Katritzky, A. R.; Perumal, S. *J. Heterocycl. Chem.* **1990**, *27*, 1737.

(13) (a) McCall, E. B.; Neale, A. J.; Rawlings, T. J. *J. Chem. Soc. Chem.* **1962**, 5288–5290. (b) Pelter, A.; Rowlands, M.; Clements, G. *Synthesis* **1987**, 51–53.

(14) Boa, A.; Archibald, S.; Pesa, N. *Chem. Commun.* **2003**, 1736.

(15) Tsujihara, K.; Furukawa, N.; Oae, S. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2153.

(16) Minakata, S.; Hotta, T.; Oderaotoshi, Y.; Komatsu, M. *J. Org. Chem.* **2006**, *71*, 7471.

(17) Kumar, G. D. K.; Baskaran, S. *Chem Commun.* **2004**, *8*, 1026.

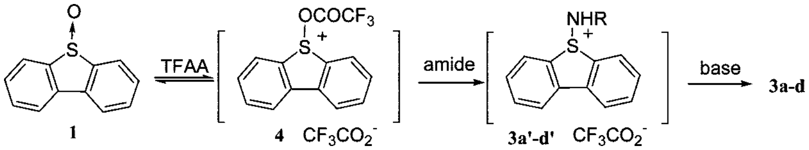
(18) (a) Meth-Cohn, O.; Vuuren, G. V. *J. Chem. Soc., Chem. Commun.* **1984**, 190–191. (b) Meth-Cohn, O.; Vuuren, G. V. *Tetrahedron Lett.* **1986**, 1105–1108.

(19) Antunes, A. M. M.; Marto, S. J. L.; Branco, P. S.; Prabhakar, S.; Lobo, A. M. *Chem. Commun.* **2001**, 405–406.

(20) Cheng, C. Y.; Lu, H. Y.; Lee, F. M.; Tam, S. W. *J. Pharm. Sci.* **1990**, *79*, 758–62.

(21) Yeung, Y.-Y.; Gao, X.; Corey, E. J. *J. Am. Chem. Soc.* **2006**, *128*, 9644–9645.

SCHEME 1. Formation of Dibenzothiophene *N*-Acylsulfilimines by the Reaction of 1 with Amides in the Presence of TFAA



SCHEME 2. Syntheses of 6a,b

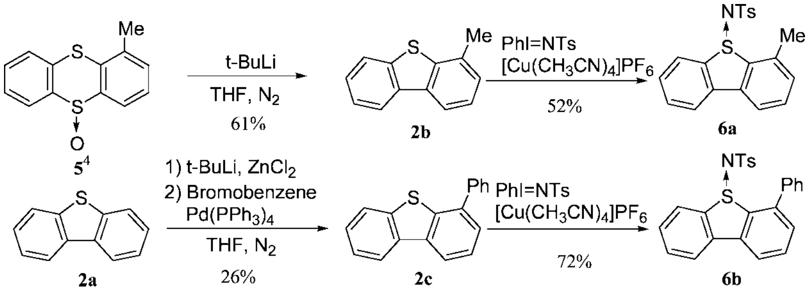
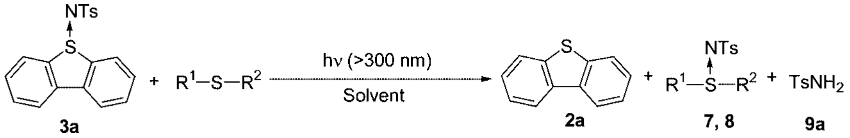


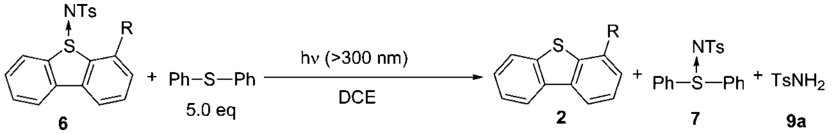
TABLE 2. Photolysis of *N*-Tosyliminodibenzothiphene in the Presence of Several Sulfides



entry	R^1	R^2	solvent	concn (mM)		time (h)	yield (%)[a]		
				sulfide	**3a**		**2a**	**7**, **8**	**9a**
1	Ph	Ph	PhH	125	25	5	99	56 (**7**)	0
2	Ph	Ph	toluene	125	25	5	98	25 (**7**)	0
3	Ph	Ph	MeCN	125	25	5	90	70 (**7**)	0
4	Ph	Ph	DCE	125	25	1.5	90	72 (**7**)	8
5	Ph	Ph	DCE	27.5	25	2	99	73 (**7**)	17
6	Ph	Ph	DCE	55	50	2	95	60 (**7**)	17
7	Ph	Ph	DCE	13.8	12.5	2	97	73 (**7**)	13
8	Ph	Me	DCE	125	25	2	99	69 (**8a**)	18
9	Me-Ph	Me	DCE	125	25	2	61	74 (**8b**)	20
10	MeO-Ph	Me	DCE	125	25	2	69	58 (**8c**)	0
11	Cl-Ph	Me	DCE	125	25	2	67	48 (**8d**)	32

[a] Isolated yield: not optimized.

TABLE 3. Photolysis of 1-Substituted *N*-Tosyliminodibenzothiphene in the Presence of Diphenyl Sulfide



entry	R	time (h)	yield (%)[a]		
			2	**7**	**9a**
1	H	2	95	72	9
2	Me	2	91	61	3
3	Ph	2	92	55	3

[a] Isolated yield: not optimized.

2.4. Photolysis of 3a–d in the Presence of Several Phosphorus Compounds. Iminophosphoranes can be generated by Staudinger reaction from organic azides and phosphorus(III) reagents[22] or by the Kirsanov reaction from primary amines and phosphorus pentahalides.[23] Both of the reactions containing the nitrene intermediates were trapped by phosphorus compound. In our unpublished studies, the reaction of triphenylphosphine with Chloramine T also was found to afford *N*-tosyliminotriphenylphosophine **11a**[24] in rather low yield and the undesired oxide was the major product.

We carried out the photolyses of *N*-substituted iminodibenzothiophene in the presence of phosphorus compound. The results are summarized in Table 5.

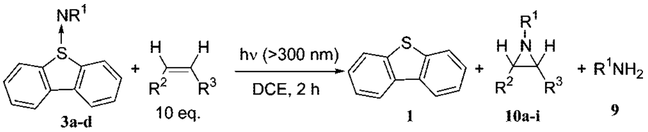
---

[22] Staudinger, H.; Meyer, J. *Helv. Chim. Acta* **1919**, 619.

[23] Kiarsanov, A. V.; Kabachnik, M. I.; Girlyarov, V. A. *Otd. Khim. Nauk SSSR* **1956**, 790.

[24] Yavari, I.; Zabarjad-Shiraz, N.; Bijanzadeh, H. R. *Phosphorus, Sulfur Silicon Relat. Elements* **2004**, *179*, 1381–1386.

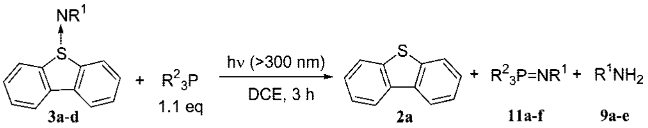
TABLE 4. Photolysis of 3a−d in the Presence of Several Olefins



entry	R^1	R^2	R^3	product	yield (%)[a]		
					1	10	9
1	Ts	$-(CH_2)_3-$		**10a**	85	57	13
2	Ts	$-(CH_2)_4-$		**10b**	94	60	22
3	Ts	$-(CH_2)_6-$		**10c**	93	66	10
4	Ts	*n*Bu	H	**10d**[18]	98	34	30
5	Ts	$-(CH_2)_3-C(O)-$		**10e**	88	31	0
6	COPh	$-(CH_2)_4-$		**10g**	94	60	22
7	COBn	$-(CH_2)_4-$		**10h**	85	57	13
8	CO^{t}Bu	$-(CH_2)_4-$		**10i**	93	66	10

[a] Isolated yields; not optimized.

TABLE 5. Photolysis of 3a−d in the Presence of Trivalent Phosphorus Compound



entry	R^1	R^2	product **11**	yield (%)[a]		
				2a	11	9
1	Ts	Ph	**11a**	>99	77	8
2	Ts	EtO	**11b**	94	64	4
3	Ts	PhO	**11c**	>99	60	9
4	PhC(O)	Ph	**11d**	95	64	0
5	BnC(O)	Ph	**11e**	90	24	0
6	^{t}BuC(O)	Ph	**11f**	86	53	0

[a] Isolated yields; not optimized.

In the photolyses of **3a** in the presence of triphenyl phosphine, iminophosphorane **11a** was formed in 77% yield as a sole product besides dibenzothiophene and **9** (entry 1). In the presence of triphenyl phosphite or triethyl phosphite, the photolyses of **3a** gave **11b**,**c**[25] and dibenzothiophene **2a** in almost the sameyields (entries 2 and 3). The photolysis of **3b** and **3d** in the presence of triphenyl phosophine gave **11d**,[25] **11f** in slightly low yields compared with those of tosyl sulfilimine **3a** (entry 1). In the case of *N*-phenylacetylsulfilimine **3c**, the reaction gave a complex mixture and the yield of **11e** was low (entry 5).

3. Conclusion

We have presented the syntheses of dibenzothiophene *N*-substituted sulfilimines and demonstrated that their photolysis proceeded smoothly in DCE in the presence of trapping reagents, such as sulfides, olefins, and phosphorus compounds, to afford the corresponding imino-transfer products, namely sulfilimines, aziridines, and iminophosphoranes, in good yields. It is suggested that the driving force of preferential S−N bond cleavage is due to the regaining of resonance energy by releasing imino substituents on sulfur, as mentioned earlier. In conclusion, in view of the easy preparation of the precursors, the recyclable use of **3** formed in the photolyses, and the relatively high yields for the desired trans-iminated product under photolytic conditions, dibenzohiophene sulfilimines were found to be very useful and versatile photolytic nitrene precursors.

We are now further continuing the study of the scope and limitations and the application for the introduction of an imino group to a variety of organic compounds under photolyses. Particularly, we are interested in introducing an imino group into fullerene molecules.

4. Experimental Section

***N*-(2-Phenylacetyl)iminodibenzothiophene (3c).** To a solution of dibenzothiophen-*S*-oxide (**1**) (100 mg, 0.5 mmol) in acetonitrile (3.0 mL) was added trifluoroacetic anhydride (315 mg, 1.5 mmol) then the reaction was stirred for 10 min at −30 °C and 2-phenylacetamide (202 mg, 1.5 mmol) was added. NaOH (0.1 N, aq) was poured into this mixture, then the mixture was evaporated in vacuo. The reaction mixture was extracted with CH_2Cl_2 (2 × 20 mL) and NaOH aq, then the organic layer was dried over $MgSO_4$, filtered, and evaporated in vacuo. Compound **3c** was purified by chromatography on silica with EtOAc/hexane. Yield 128 mg, 80%; mp 133−135 °C (from CH_2Cl_2−hexane), ν_{max} (KBr)/cm^{-1} 751, 1131, 1291, 1307, 1333, 1426, 1491, 1556, 1599, 2927, 3030; ^{1}H NMR (400 MHz) δ 3.73 (2H, s), 7.20−7.39 (5H, m), 7.50 (2H, dt, J = 7.6, 0.8 Hz), 7.63 (2H, dt, J = 7.6, 0.8 Hz), 7.88 (2H, d, J = 8.0 Hz), 8.12 (2H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz) δ 43.8, 122.2, 126.2, 128.2, 128.6, 129.2, 129.8, 132.3, 137.1, 137.7, 138.2, 183.9. Anal. Calcd for $C_{20}H_{15}NOS$: C, 75.68; H,4.76; N, 4.41. Found: C, 75.93; H, 4.78; N, 4.40. LR-MS (M − 91) 226.

***N*-(Pivaloyl)iminodibenzothiophene (3d).** To a solution of dibenzothiophen-*S*-oxide (**1**) (100 mg, 0.5 mmol) in acetonitrile (3.0 mL) was added trifluoroacetic anhydride (210 mg, 1.0 mmol) then the reaction was stirred for 10 min at −30 °C and pivalamide (75 mg, 0.75mmol) was added. NaOH (0.1 N) was poured into this mixture, which was then evaporated in vacuo. The reaction mixture was extracted with CH_2Cl_2 (2 × 20 mL) and NaOH aq, then the organic layer was dried over $MgSO_4$, filtered, and evaporated in vacuo. Compound **3d** was purified by chromatography on silica gel with EtOAc/hexane. Yield 33.6 mg, 24%; mp 142−144 °C (from EtOAc−hexane), ν_{max} (KBr)/cm^{-1} 735, 757, 1195, 1308, 1447, 1476, 1536, 2859, 2922, 2947; ^{1}H NMR (400 MHz) δ 1.24 (9H, s), 7.51 (2H, t, J = 7.2 Hz), 7.63 (2H, t, J = 7.6 Hz), 7.90 (2H, d, J = 8.0 Hz), 8.12 (2H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz) δ 28.7, 40.1, 122.1, 128.4, 129.6, 132.0, 138.1, 138.5, 192.1. Anal. Calcd for $C_{17}H_{17}NOS$: C, 72.06; H, 6.05; N, 4.94. Found: C, 72.34; H, 6.09; N, 5.06. LR-MS (M^+ − 57) 226.

4-Methyl-5-*N*-(*p*-toluenesulfonyl)iminodibenzothiophene (6a). To a solution of (*N*-tosyl)iminophenyliodinane (1160 mg, 3.11 mmol) in CH_3CN was added compound **2b** (560 mg, 2.82 mmol) and tetrakis(acetonitrile)copper(I) hexafluorophosphate (105.2 mg, 0.282 mmol). This reaction mixture was allowed to stand for 75 min at 0 °C under N_2 atmosphere. Compound **6a** was purified by chromatography on silica with EtOAc/hexane (2/1). Yield 52%, mp 185−186 °C; ν_{max} (KBr)/cm^{-1} 930, 1141, 1300, 2923, 3016, 3058; ^{1}H NMR (400 MHz) δ 2.38 (3H, s), 2.41 (3H, s), 7.19−7.23 (3H, m), 7.41 (1H, dt, J = 7.2, 1.2 Hz), 7.53 (1H, t, J = 8.0 Hz), 7.59−7.63 (2H, m), 7.70 (1H, t, J = 7.6 Hz), 7.74 (2H, d, J = 8.4 Hz), 7.83 (2H, d, J = 8.4 Hz); ^{13}C NMR (100 MHz) δ 18.8, 21.5, 120.1, 122.4, 126.7, 127.4, 129.2, 129.9, 130.1, 131.5, 132.8, 133.3, 137.6, 137.8, 137.9, 139.7, 140.9, 142.0. Anal. Calcd for $C_{20}H_{17}NO_2S_2$: C, 65.37; H, 4.66; N, 3.81. Found: C, 64.91; H, 4.67; N, 3.81.

4-Phenyl-5-*N*-(*p*-toluenesulfonyl)iminodibenzothiophene (6b). To a solution of (*N*-tosyl)iminophenyliodinane (473 mg, 1.27 mmol) in CH_3CN was added compound **2c** (300 mg, 1.15 mmol) and

---

(25) Laszlo, P.; Polla, E. *Tetrahedron Lett.* **1984**, *25*, 4651–4654.

(26) Gentle, C. A.; Bugg, T. D. H. *J. Chem. Soc., Perkin Trans. 1* **1999**, *10*, 1279–1286.

tetrakis(acetonitrile)copper(I) hexafluorophosphate (42.8 mg, 0.115 mmol). This reaction mixture was allowed to stand for 75 min at 0 °C under N_2 atmosphere. Compound **6b** was purified by chromatography on silica with EtOAc/hexane (2/1). Yield 72%, mp 159−160 °C; ν_{max} (KBr)/cm^{-1} 945, 1142, 1295, 3015, 3062; ^{1}H NMR (400 MHz) δ 2.37 (3H, s), 7.01 (2H, d), 7.30 (2H, d, J = 8.0 Hz), 7.35−7.42 (2H, m), 7.48−7.50 (2H, m), 7.61 (1H, dt, J = 7.6, 1.6 Hz), 7.70 (1H, t, J = 7.6 Hz), 7.74 (1H, d, J = 7.2 Hz), 7.85−7.89 (5H, m); ^{13}C NMR (100 MHz) δ 21.4, 121.2, 122.3, 126.3, 127.6, 128.3, 128.8, 129.0, 131.4, 131.4, 132.7, 133.4, 136.7, 137.5, 138.5, 139.1, 140.9, 141.2, 143.4. Anal. Calcd for $C_{25}H_{19}NO_2S_2$: C, 69.90; H, 4.46; N, 3.27. Found: C, 69.41; H, 4.48; N, 3.27

Supporting Information Available: Experimental procedures and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

JO800604T