

1-Imino and 1,1-Diimino Derivatives of 3,4-Di-*tert*-butylthiophene

Takashi Otani, Yoshiaki Sugihara, Akihiko Ishii, and Juzo Nakayama*

Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338-8570, Japan

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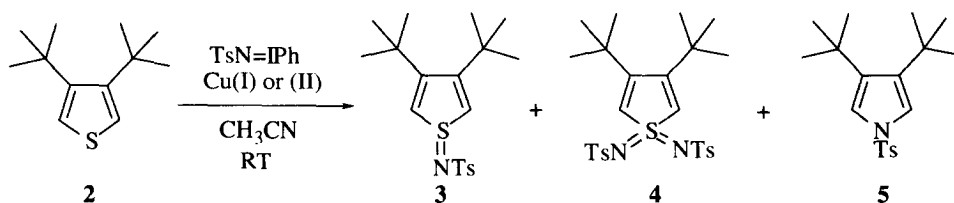
Abstract: The reaction of 3,4-di-*tert*-butylthiophene (**2**) with *N*-[(*p*-tolylsulfonyl)imino]phenyliodinane (TsN=IPh) in the presence of Cu(MeCN)₄PF₆ in MeCN at room temperature provided 3,4-di-*tert*-butyl-1-[(*p*-tolylsulfonyl)imino]-1,1-dihydrothiophene (**3**), 3,4-di-*tert*-butyl-1,1-bis[(*p*-tolylsulfonyl)imino]-1,1-dihydrothiophene (**4**), and 1-(*p*-tolylsulfonyl)-3,4-di-*tert*-butylpyrrole (**5**) as the principal products. The use of **2** in a large excess gave **3** in a better yield of 61%. Results of the X-ray crystallographic analyses of **3** and **4** are also reported.

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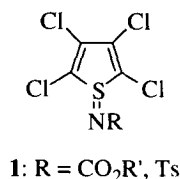
The chemistry of sulfilimines and sulfone diimines, where the oxygen atom(s) of sulfoxides and sulfones are replaced by imino group(s), has been studied in some detail.¹ Attention being given to the sulfur atom of thiophenes, the chemistry of thiophene 1-oxides is a matter of recent much interest^{2c} and that of thiophene 1,1-dioxides has been fully established,^{2a,b} but 1-imino and 1,1-diimino derivatives of thiophenes (sulfilimines and sulfone diimines, respectively) have been scarcely studied.³ Particularly, the latter species still remain to be synthesized. Compounds **1**, which were obtained by thermolyses of azides in tetrachlorothiophene, are the only reported example of sulfilimines derived from monocyclic thiophenes.^{3a,b} The successful synthesis of **1** is exceptional since replacement of one or two chlorine atoms of tetrachlorothiophene by other substituents failed to provide the corresponding sulfilimines by this method.^{3a,b} Other thermolysis studies of azides in thiophenes also failed to give sulfilimines.⁴⁻⁶ This would be attributed to the probable thermal instability of the sulfilimines and the forcing conditions required for the thermolysis of azides (130–150 °C).³⁻⁶ Sulfilimines and sulfone diimines of thiophenes would be stabilized by introduction of bulky substituents into the double bond part of the ring as so with thiophene 1-oxides⁷ and thiophene sulfoximides.⁸ We therefore examined their preparation by reaction of sterically congested 3,4-di-*tert*-butylthiophene (**2**)⁹ with *N*-[(*p*-tolylsulfonyl)imino]phenyliodinane (TsN=IPh)¹⁰ that generates the tosyl nitrene or its equivalent at lower temperature in the presence of a Cu(I or II) catalyst.¹¹ This led to not only the successful synthesis of the sulfilimine **3** but also synthesis of the first sulfone diimine **4**.

Thus, **2** and TsN=IPh of varying molar ratios were allowed to react in the presence of 5 mmol% of Cu(CH₃CN)₄PF₆ [(Cu(I))¹² or Cu(OTf)₂ [Cu(II)] in acetonitrile. The reaction took place at room temperature smoothly. Purification of the mixture provided the expected sulfilimine **3**^{13,14} with unexpected formation of the sulfone diimine **4**^{13,14} and the pyrrole **5**⁵ (Table 1). Compounds **6**, **7**, and TsNH₂ were also isolated in small amounts.^{13,14} Structures of **3**, **4**, and **7** were determined by X-ray crystallographic analysis.^{15,16} Better results were attained by using Cu(I) as the catalyst rather than Cu(II). The yield of **3** increased with an increasing molar ratio of **2**; a satisfactory yield of 61% was attained by use of 20 molar amounts of **2**. Both **3** and **4** are thermally stable and melted at 130.0–131.0 and 155.0–155.5 °C, respectively, without decomposition.

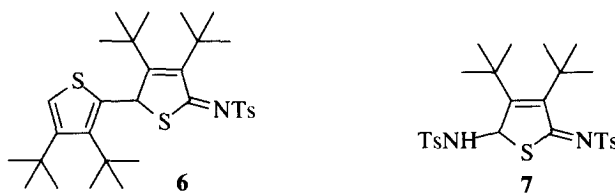
(E-mail: nakaj@sacs.sv.saitama-u.ac.jp)

Table 1. Reactions of **2** with TsN=IPh under a Variety of Conditions.

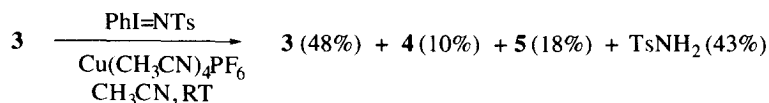
Entry	Molar Ratio 2/TsN=IPh	Catalyst ^b	Isolated Yield (%) ^a				
			3	4	5	6	7
1	2.5	Cu(I)	23	9	9	2	+ ^c
2	5.0	Cu(I)	38	18	10	3	+ ^c
3	5.0	Cu(II)	32	8	4	3	3
4	7.5	Cu(I)	50	9	10	4	+ ^c
5	20	Cu(I)	61	7	5	3	4



^a Based on TsN=IPh. ^b Cu(I) = Cu(CH₃CN)₄PF₆, Cu(II) = Cu(OTf)₂. ^c No effort was made to isolate **7** (detected by tlc)



Most probably, the sulfone diimine **4** would be formed by further reaction of **3** with TsN=IPh. A separate reaction of **3** with TsN=IPh in the presence of 5 mmol% of Cu(I) gave **4** in low yield (10%) with recovery of **3** in 48% yield. The pyrrole **5** (18%) and TsNH₂ (43%) were also formed. To our knowledge, the formation of sulfone diimines by reaction of sulfides with TsN=IPh is unprecedented. We previously reported that the pyrrole **5** was formed, though in a low yield, by thermolysis of tosyl azide in **2** (150 °C).⁵ It is noteworthy that **5** was formed even at room temperature by reactions of **2** and **3** with TsN=IPh. The sulfilimine **3** is not converted to **5** thermally; **3** was recovered when heated at 160 °C in benzene in a sealed tube for 3 h. Also, the conversion of **3** to **5** was not brought about by the action of the Cu(I) catalyst at room temperature. Apparently, an unknown catalytic mechanism that promotes the conversion of **3** to **5** exists. A clear-cut mechanism for the formation of **6** and **7** is not available currently, though many tentative explanations are possible.



ORTEP drawing structures of **3** and **4** are given in Figures 1 and 2, respectively, along with the relevant

bond lengths and angles data.¹⁶ In both compounds, although the four carbon atoms of the thiophene ring form a quasi-plane, their C2-C3 (1.53-1.54 Å) and C1-C2 (C3-C4) bond lengths (1.33-1.34 Å) are almost equal to the common single and double bond lengths, respectively, indicating the presence of bond alternation, that is, the loss of the aromaticity of the thiophene ring. On the whole, the geometry of sulfilimine **3** is similar to that of thiophene 1-oxides^{7b,c} with a pyramidal configuration of the sulfur atom and with the S-N bond length of 1.60 Å. The pyramidal sulfur geometry and the bond lengths data lead to the conclusion that **3** is not aromatic. On the other hand, in the sulfone diimine **4**, the thiophene ring is nearly planar as so with most thiophene 1,1-dioxides.¹⁷ The S-N1 and S-N2 bond lengths of **4** are 1.55 Å and are nearly equal to the bond length (1.54 Å) of the common S-N bonds that are conventionally expressed by a double bond.¹⁸

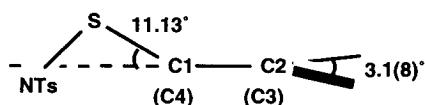
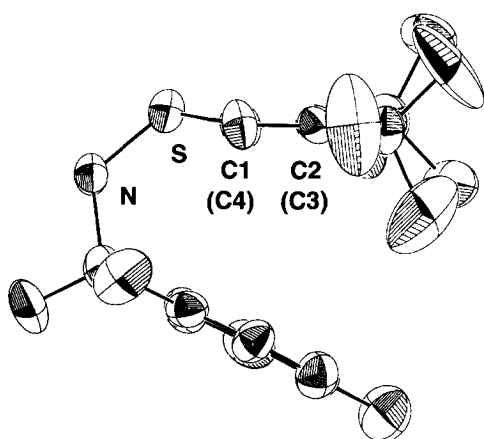


Figure 1. ORTEP diagram of **3**. Selected bond lengths: S-N, 1.595(7); S-C1, 1.744(7); S-C4, 1.742(8); C1-C2, 1.332(11); C2-C3, 1.535(10); C3-C4, 1.329(10) Å. Bond angles: C1-S-C4, 90.7(4); S-C1-C2, 113.6(6); C1-C2-C3, 109.9(7); C2-C3-C4, 111.7(7); C3-C4-S, 112.6(6)°.

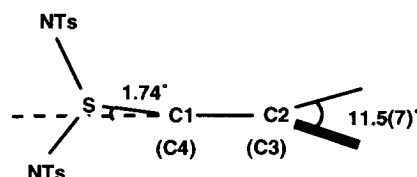
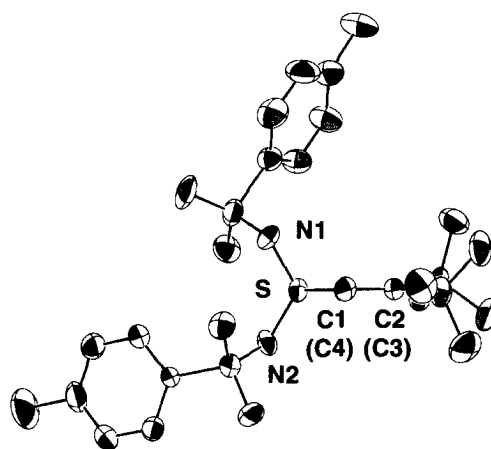


Figure 2. ORTEP diagram of **4**. Selected bond lengths: S-N1, 1.551(6); S-N2, 1.557(5); S-C1, 1.737(7); S-C4, 1.728(7); C1-C2, 1.339(10); C2-C3, 1.524(11); C3-C4, 1.343(9) Å. Bond angles: N1-S-N2, 121.5(3); C1-S-C4, 93.1(4); S-C1-C2, 111.7(5); C2-C3-C4, 111.7(6); C3-C4-S, 111.7(5)°.

In conclusion, we have succeeded in the preparation of the sulfilimine and sulfone diimine derivatives of 3,4-di-*tert*-butylthiophene and their X-ray crystallographic analyses. We are currently investigating the desilylation of **3** and **4** in order to obtain the *N*-unsubstituted parent compounds¹⁹ and the application of the present reaction to other thiophenes.

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- [13] All new compounds gave satisfactory elemental analysis results.
- [14] **3**: 130-131 °C (cyclohexane); ¹H NMR (400 MHz, CDCl₃) δ = 1.37 (s, 18H), 2.40 (s, 3H), 6.70 (s, 2H), 7.24 (d, *J* = 8 Hz, 2H), 7.76 (d, *J* = 8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ = 21.4 (CH₃), 31.8 (CH₃), 36.4 (C), 127.0 (CH), 128.4 (CH), 129.2 (CH), 140.3 (C), 142.2 (C), 161.8 (C). **4**: mp 155.0-155.5 °C (Et₂O/hexane); ¹H NMR (400 MHz, CDCl₃) δ = 1.38 (s, 18H), 2.40 (s, 6H), 7.13 (s, 2H), 7.21 (d, *J* = 8 Hz, 4H), 7.72 (d, *J* = 8 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃) δ = 21.6 (CH₃), 31.3 (CH₃), 36.7 (C), 125.9 (CH), 126.9 (CH), 129.3 (CH), 139.6 (C), 143.2 (C), 160.4 (C). **6**: mp 140.0-141.0 °C (pentane); ¹H NMR (400 MHz, CDCl₃) δ = 1.34 (s, 9H), 1.47 (s, 9H), 1.51 (s, 9H), 1.63 (s, 9H), 2.42 (s, 3H), 6.57 (s, 1H), 7.07 (s, 1H), 7.29 (d, *J* = 8 Hz, 2H), 7.85 (d, *J* = 8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ = 21.6 (CH₃), 31.7 (CH₃), 33.3 (CH₃), 34.58 (CH₃), 34.61 (CH₃), 36.9 (C), 37.1 (C), 37.3 (C), 38.6 (C), 57.2 (CH), 121.3 (CH), 127.0 (CH), 129.3 (CH), 137.5 (C), 138.2 (C), 143.2 (C), 145.7 (C), 149.0 (C), 152.1 (C), 167.0 (C), 183.8 (C). **7**: mp > 167 °C (dec) (Et₂O/hexane); ¹H NMR (400 MHz, CDCl₃) δ = 1.37 (s, 9H), 1.47 (s, 9H), 2.42 (s, 3H), 2.50 (s, 3H), 4.38 (d, *J* = 12 Hz, 1H), 6.04 (d, *J* = 12 Hz, 1H), 7.27 (d, *J* = 8 Hz, 2H), 7.40 (d, *J* = 8 Hz, 2H), 7.74 (d, *J* = 8 Hz, 2H), 7.76 (d, *J* = 8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ = 21.6 (CH₃), 21.8 (CH₃), 31.6 (CH₃), 32.3 (CH₃), 36.9 (C), 37.7 (C), 67.0 (CH), 127.1 (CH), 127.8 (CH), 129.4 (CH), 130.4 (CH), 135.5 (C), 137.3 (C), 143.7 (C), 145.3 (C), 149.9 (C), 163.5 (C), 181.2 (C); IR (KBr) 3216 cm⁻¹ (N-H).
- [15] Crystallographic analysis of **7** will be described elsewhere.
- [16] Crystal structure data for **3**: C₁₉H₂₇NO₂S₂, *M_r* = 365.56, triclinic, P-1, *a* = 9.696 (1), *b* = 14.071 (3), *c* = 15.614 (4) Å, α = 105.811 (9), β = 100.32 (1), γ = 98.07 (1)°, *V* = 1975.9(7) Å³, *Z* = 4, *D_c* = 1.229 gcm⁻³, μ = 2.68 mm⁻¹, λ = 0.71073 Å, *T* = 298 K, crystal dimensions (0.29 x 0.08 x 0.10 mm), Mac Science DIP3000 diffractometer, 3087 observed reflections, *R* = 0.079, *wR* = 0.075, *S* = 1.526. Crystal structure data for **4**: C₂₆H₃₄N₂O₄S₃, *M_r* = 534.77, monoclinic, *P*₂₁/*n*, *a* = 10.246 (2), *b* = 11.848 (1), *c* = 22.677 (3) Å, β = 95.132 (7)°, *V* = 2741.8(6) Å³, *Z* = 4, *D_c* = 1.295 gcm⁻³, μ = 2.91 mm⁻¹, λ = 0.71073 Å, *T* = 298 K, crystal dimensions (0.16 x 0.08 x 0.08 mm), Mac Science DIP3000 diffractometer, 2859 observed reflections, *R* = 0.071, *wR* = 0.071, *S* = 2.148.
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