Reaction of 3,4-Di-*t*-butylthiophene 1-Oxide with 2-Methylene-1,3-dimethylimidazolidine: Methylene Transfer and [4+4] Dimerization

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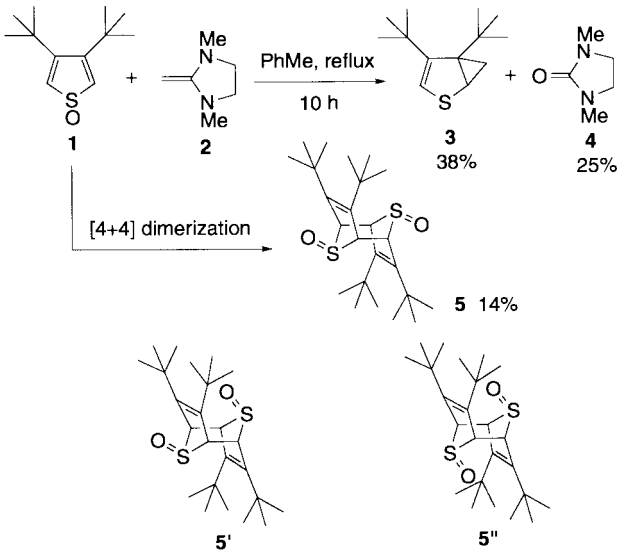
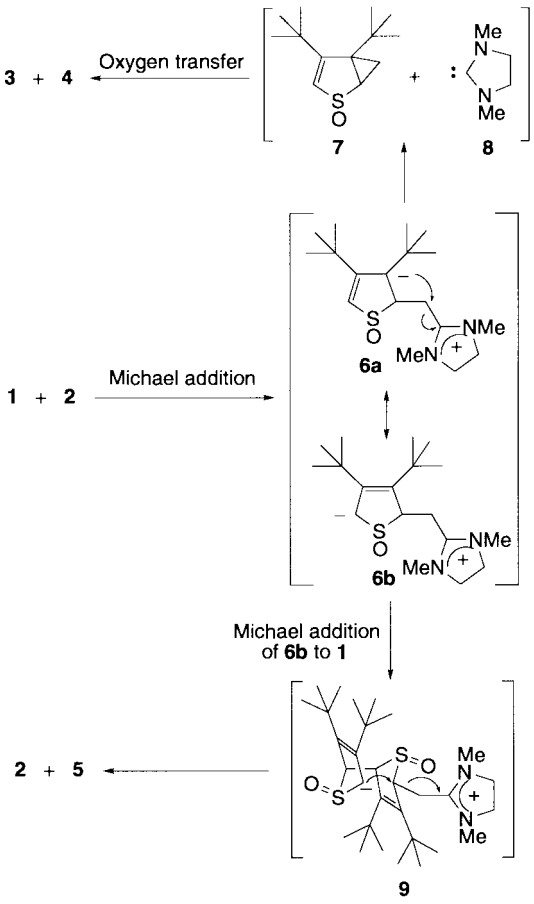
The reaction of 3,4-di-*t*-butylthiophene 1-oxide (**1**) with 2-methylene-1,3-dimethylimidazolidine (**2**) gave 4,4a-di(*t*-butyl)-1a,4a-dihydro-1*H*-cyclopropa[*b*]thiophene and 1,3-dimethyl-2-imidazolidinone through a methylene transfer from **2** to **1**, in addition to a [4+4] cyclodimerization product of **1**.

Recent reports have revealed that thiophene 1-oxides act as a diene toward a variety of electron-deficient or angle-strained dienophiles to give [4+2] cycloadducts. Reactions take place with a high π-facial selectivity, in which dienophiles add thiophene 1-oxides with *endo*-orientation from *syn*-direction respect to the S–O bond.[1,2] However, the stereochemical course of reactions of thiophene 1-oxides with electron-rich alkenes has not hitherto been reported. We were therefore interested in the stereochemistry of the reaction of 3,4-di-*t*-butylthiophene 1-oxide (**1**)[3] with a highly electron-rich enediamine, 2-methylene-1,3-dimethylimidazolidine (**2**).[4] Here we report that the reaction proceeded through an unprecedented methylene transfer from **2** to **1** to give 4,4a-di(*t*-butyl)-1a,4a-dihydro-1*H*-cyclopropa[*b*]thiophene (**3**) and 1,3-dimethyl-2-imidazolidinone (**4**) without formation of the expected [2+4] adduct. In addition, a [4+4] cyclodimerization of **1** took place to give a highly congested compound **5** with a rigid framework.

Thus, heating **1** and **2** in refluxing toluene for 10 h afforded **3** and **4** in 38 and 25% yields, respectively, in addition to the dimer **5** in 14% yield. The two methylene hydrogens of **3** are much shielded and resonated at δ 0.23 and 1.19 as a doublet of doublet, thus indicating that the methylene carbon constitutes a part of the cyclopropane ring.[5] The mass spectrum of **5** showed a molecular ion peak at *m/z* 424 ($C_{24}H_{40}O_2S_2$), suggesting **5** being a dimer of **1**. The ^{1}H NMR spectrum exhibited only two singlets at δ 1.35 and 3.96 with an intensity ratio of 9:1 and the ^{13}C NMR spectrum showed only four peaks in accordance with the given structure, which possesses two equatorial S–O bonds.[6,7] An isomeric compound **5'** is ruled out unequivocally by the NMR data. The formation of the other isomeric compound **5"**, bearing two axial S–O bonds, would be least probable due to 1,3-diaxial nonbonded repulsions.

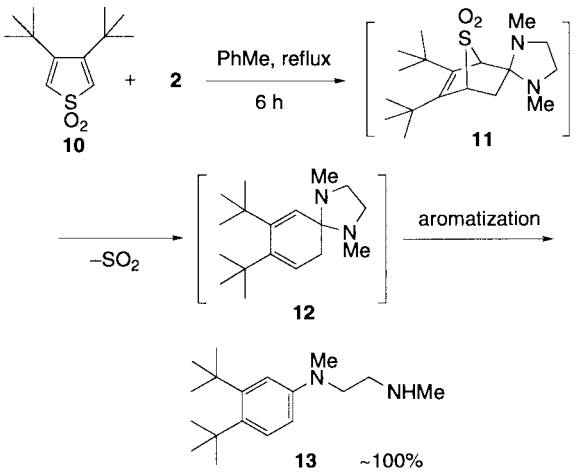
The formation of **3**–**5** will be best explained as follows. The enediamine **2**, which has ylidic properties,[4] adds **1** to give the Michael adduct **6**[8] but not the expected Diels–Alder adduct. An intramolecular cyclization of **6**, assisted by contribution of the canonical structure **6a**, would give rise to **7** with elimination of the carbene **8**. Recently, the carbene **8** has been shown to serve as a leaving group.[9] An oxygen transfer from **7** to **8**, presumably in a solvent cage, would produce **3** and **4**. To our knowledge, this is the first example that the methylene of an alkene was transferred to the double bond of a substrate for cyclopropanation.[10–12] Meanwhile, the Michael addition of **6** to





the 1-oxide **1**, assisted by contribution of the canonical structure **6b**, affords **9**, which then furnishes the dimer **5** with elimination of **2**.[13] It should be stressed here that the presence of **2** is truly essential for the dimerization of **5**; heating **1** alone in refluxing chlorobenzene for 24 h did not give **5** even in a trace amount and heating under more forcing conditions resulted in the deoxidization principally to give 3,4-di-*t*-butylthophene.

For comparison, the reaction of 3,4-di-*t*-butylthiophene 1,1-dioxide (**10**) with **2** was then examined. Unexpectedly again, the reaction produced an *o*-di-*t*-butylbenzene derivative **13**[14] quantitatively. The initial step of the reaction would involve a [4+2] cycloaddition to give the adduct **11**, followed by spontaneous extrusion of SO_2 to afford **12**. Finally, aromatization of **12** would furnish **13** with ring-opening of the five-membered ring. It is thus concluded that the 1,1-dioxide **10**, which is a more electron-deficient diene than the 1-oxide **1**, undergoes a Diels–Alder reaction of inverse electron-demand with an electron-rich alkene **2**.[15] In addition, the present reaction would be promising as a synthetic method for *o*-di-*t*-butylbenzene derivatives, which are otherwise difficult to prepare.[16]



References and Notes

1 For reviews, J. Nakayama and Y. Sugihara, *Sulfur Reports*, **19**, 349 (1996); J. Nakayama, *Sulfur Reports*, **22**, 123 (2000).

2 A. M. Naperstkow, J. B. Macaulay, M. J. Newlands, and A. G. Fallis, *Tetrahedron Lett.*, **30**, 5077 (1989); N. H. Werstiuk and J. Ma, *Can. J. Chem.*, **72**, 2493 (1994); Y.-Q. Li, M. Matsuda, T. Thiemann, T. Sawada, S. Mataka, and M. Tashiro, *Synlett*, **1996**, 461; Y.-Q. Li, T. Thiemann, T. Sawada, S. Mataka, and M. Tashiro, *J. Org. Chem.*, **62**, 7926 (1997); Y.-Q. Li, T. Thiemann, K. Mimura, T. Sawada, S. Mataka, and M. Tashiro, *Eur. J. Org. Chem.*, **1998**, 1841; N. Furukawa, S.-Z. Zhang, E. Horn, O. Takahashi, and S. Sato, *Heterocycles*, **47**, 793 (1998).

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5 **3**: bp 92 °C/3 mmHg (bulb-to-bulb distillation); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.23 (1H, d/d, *J* = 5.3/5.1 Hz), 1.05 (9H, s), 1.19 (1H, d/d, *J* = 8.3/5.3 Hz), 1.25 (9H, s), 2.73 (1H, d/d/d, *J* = 8.3/5.1/2.1 Hz), 5.68 (1H, d, *J* = 2.1 Hz); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 13.4, 27.1, 29.6, 31.8, 32.6, 36.3, 46.3, 119.4 and 150.3; MS *m/z* 210 (M^+), 195, 153, 139, 121, 111, 57. HRMS Calcd for $C_{13}H_{22}S$: 210.1442. Found: 210.1455.

6 **5**: mp > 310 °C (sublimed without melting); colorless needles; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.35 (36H, s) and 3.96 (4H, s); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 31.8, 34.4, 66.3 and 136.5; IR (KBr) 1050 cm^{-1} (S–O); MS *m/z* 424 (M^+), 367, 311. Anal. Calcd for $C_{24}H_{40}O_2S_2$: C, 67.87; H, 9.49%. Found: C, 67.86; H, 9.52%.

7 X-ray crystallographic analysis supported the structure **5**, however, the number of observed reflections used for the analysis was too small to provide the reliable data.

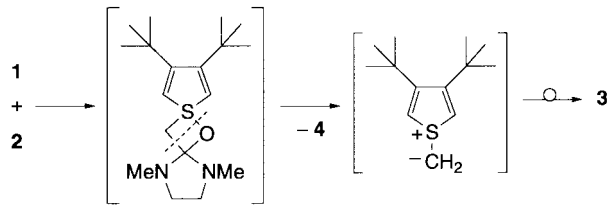
8 For capability of **1** as a Michael acceptor, see T. Otani, Y. Sugihara, A. Ishii, and J. Nakayama, *Chem. Lett.*, **2000**, 744.

9 J. Nakayama, K. Akimoto, and Y. Sugihara, *Tetrahedron Lett.*, **39**, 5587 (1998); J. Nakayama, T. Kitahara, Y. Sugihara, and A. Ishii, *Chem. Lett.*, **1999**, 187; J. Nakayama, L. Zhao, T. Otani, Y. Sugihara, and A. Ishii, *Chem. Lett.*, **2000**, 1248.

10 N. Kuhn, H. Bohnen, J. Kreutzberg, D. Bläser, and R. Boese, *J. Chem. Soc., Chem. Commun.*, **1993**, 1136.

11 Compound **2**[4] and its unsaturated derivative (1,3,4,5-tetramethyl-2-methyleneimidazoline)[9] were reported to be ylidic mainly based on physical and chemical properties (^{1}H and ^{13}C NMR and X-ray diffraction analyses and formation of complexes with BF_3 and $Mo(CO)_5$).

12 The following may provide an alternative mechanism for the formation of **3** and **4**.



13 This is the first example of a [4+4] dimerization of thiophene 1-oxides. Generally, thiophene 1-oxides dimerize in a [2+4] manner.[1]

14 **13**: bp 122 °C/0.6 mmHg (bulb-to-bulb distillation); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.42 (1H, broad m), 1.52 (9H, s), 1.55 (9H, s), 2.46 (3H, s), 2.80 (2H, t, *J* = 6.4 Hz), 2.93 (3H, s), 3.41 (2H, t, *J* = 6.4 Hz), 6.57 (1H, d/d, *J* = 8.8/2.9 Hz), 7.00 (1H, d, *J* = 2.9 Hz), 7.46 (1H, d, *J* = 8.8 Hz); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 34.5, 34.8, 36.4, 36.5, 37.6, 38.2, 49.5, 52.8, 109.6, 113.7, 130.3, 136.5, 146.8, 149.2. HRMS Calcd for $C_{18}H_{32}N_2$: 276.2566. Found: 276.2562.

15 For Diels–Alder reactions of thiophene 1,1-dioxides including **10**, see a review J. Nakayama and Y. Sugihara, *Top. Curr. Chem.*, **205**, 131 (1999).

16 For preparation of *o*-di-*t*-butylbenzene derivatives, see J. Nakayama, R. Hasemi, K. Yoshimura, Y. Sugihara, S. Yamaoka, and N. Nakamura, *J. Org. Chem.*, **63**, 4912 (1998) and references cited therein.