Preparation of (Phenyloxazolo)-3-sulfolene. A Precursor for (Phenyloxazolo)-*o*-quinodimethane

Ta-shue Chou,* Hong-Chuan Chen, and Chung-Ying Tsai

Institute of Chemistry, Academia Sinica, Taipei, Taiwan, and Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC

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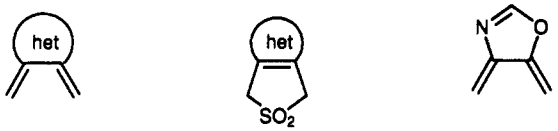
There has been growing interest in the study of heteroaromatic *o*-quinodimethanes **1**.[1] Among the several known methods for their preparation, the method involving extrusion of SO_2 from heteroaromatic-fused 3-sulfolenes **2** is the best for synthetic purposes. There are several advantages to this approach: (a) removal of SO_2 from 3-sulfolenes requires moderate temperatures, normally between 100–180 °C,[2] (b) derivatives of 3-sulfolenes are easily prepared by direct deprotonation/substitution processes,[3] and (c) heteroaromatic-fused 3-sulfolenes of similar structure can be synthesized from a common intermediate. By means of this strategy, we have prepared thieno- and pyrrolo-3-sulfolenes from a 1,4-dicarbonyl compound;[4] pyrazolo- and isoxazolo-3-sulfolenes from a 1,3-dicarbonyl compound;[5] and thieno-, pyrrolo-, and furano-3-sulfolenes from 4-bromo-3-chloro-2-sulfolene.[6] In this paper, we wish to report the synthesis and reactions of oxazolo-3-sulfolenes.

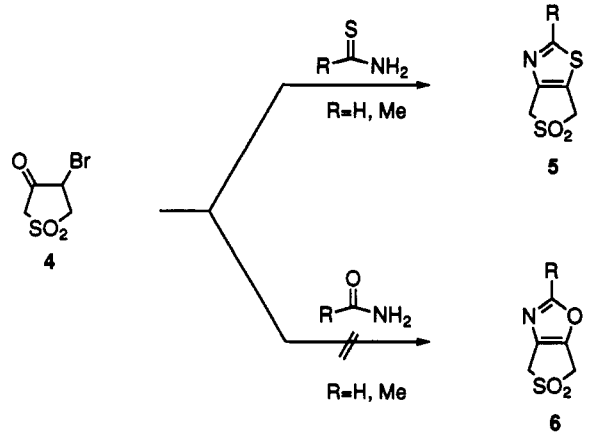


1 **2** **3**

Oxazolo-*o*-quinodimethane **3** has been generated by flash vacuum pyrolysis at 700 °C from 5-[[(*p*-chlorobenzoyl)-oxy]methyl]-4-methyloxazole.[7] Highly reactive species **3** has been trapped as the SO_2 or PhSH adduct in low yield. In addition, the reaction of **3** with methyl acrylate gave the corresponding Diels–Alder adduct, but the yield was not reported.

We recently prepared thiazolo-3-sulfolenes **5** (Scheme 1)[8] in one step from 4-bromo-3-sulfolanone **4**, which should also be an intermediate for the synthesis of oxazolo-3-sulfolenes. To our disappointment, treatment of compound **4** with formamide or acetamide under various conditions failed to yield the desired oxazolo-3-sulfolene **6**.

Scheme 1



We then turned to epoxide **7**,[9] from which bromo ketone **4** could be prepared, as the starting material (Scheme 2). Amino alcohol **8** was prepared by the reaction of **7** with NH_4OH by means of a known procedure.[9] Attempted selective N-acylation of **8** with 1 equiv of benzoyl chloride gave a mixture of desired product **10a** and *N*,*O*-diacylated product **9a**; the mixture required tedious separation. Therefore, compound **8** was first completely diacylated, and then the ester moiety of **9a** was selectively hydrolyzed with $NaHCO_3$ in MeOH. The resulting hydroxy amide **10a** was not isolated but directly oxidized with Jones' reagent to ketone **11a**. Several other amidosulfolanones, **11b–d**, were prepared by the same reaction sequence. In the case of **9e**, selective hydrolysis was not achieved with methanolic $NaHCO_3$.

Treatment of **11** with acetic anhydride, sulfuric acid, thionyl chloride, phosphorus pentoxide, or polyphosphoric acid gave complex mixtures that did not contain the desired oxazolo-3-sulfolenes. When compound **11a** was heated with PCl_5 in refluxing $CHCl_3$, unexpected product **12a** was obtained in good yield. Dichlorides **12b,c** were obtained under the same conditions from **11b,c** (Scheme 3). The unexpected result was not totally disappointing because, knowing that many bis(halomethyl) heteroaromatics have been converted to the corresponding *o*-quinodimethanes,[10] we expected dichlorides **12** to serve as precursors to **13**. When compound **12a** was treated with NaI in DMF in the presence of *N*-phenylmaleimide or dimethyl fumarate, Diels–Alder cycloadducts **14** (22%) and **15** (10%) were obtained, indicating that oxazolo-*o*-

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(11) 2,2,5,5-Tetrasubstituted 3-sulfolenes normally lose SO_2 with great difficulty under thermal conditions. See: (a) Chou, T. S.; Chang, L. T.; Tso, H. H. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1039. (b) Chou, T. S.; Chang, S. Y. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1459.

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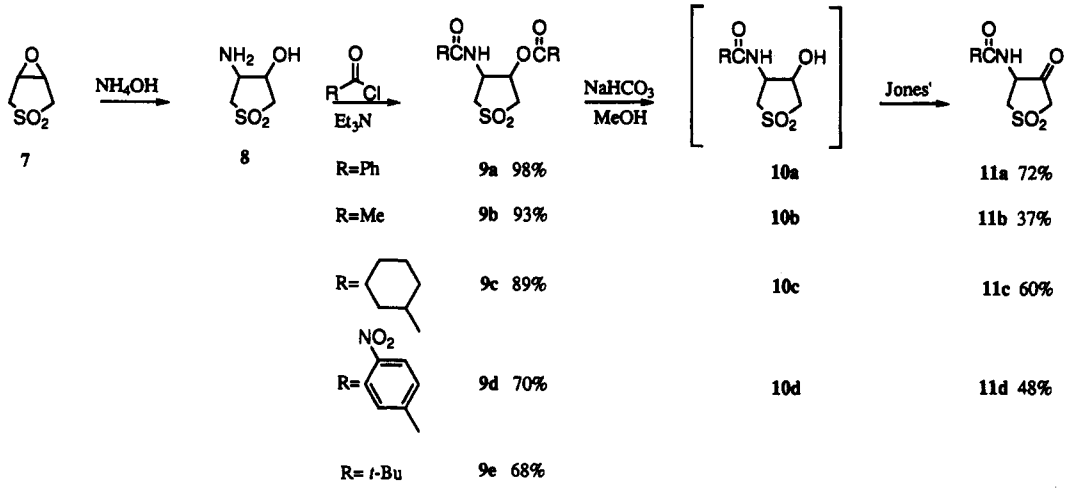
Scheme 2



Scheme 3

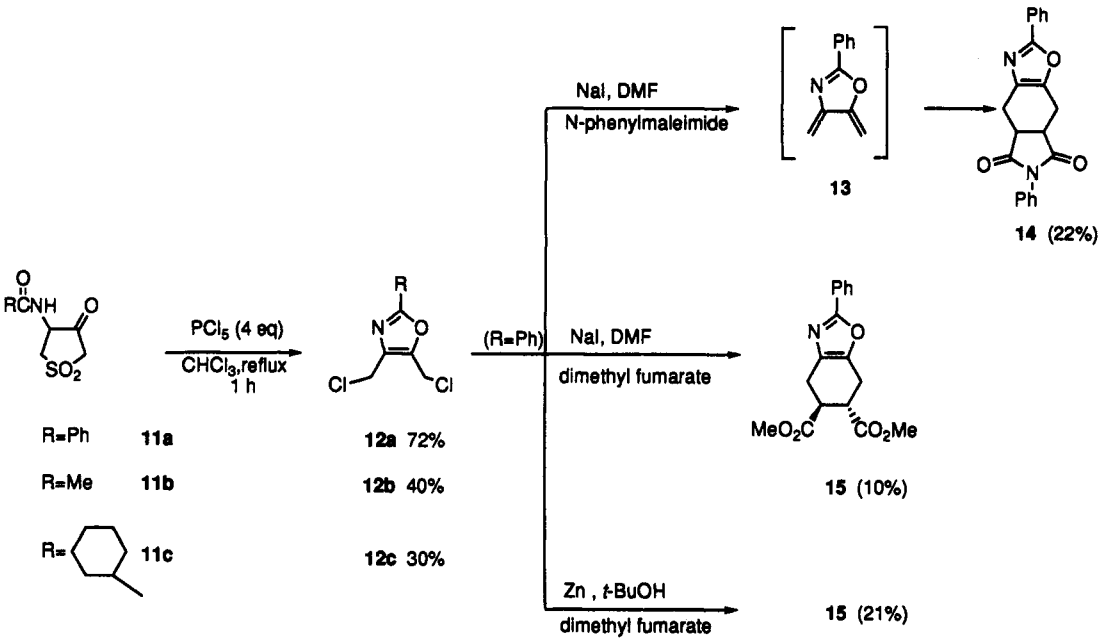
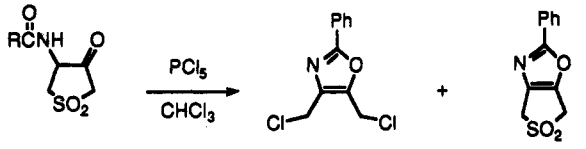


Table 1. Reaction of 4-Benzamido-3-sulfolanone 11a with PCl_5 in $CHCl_3$



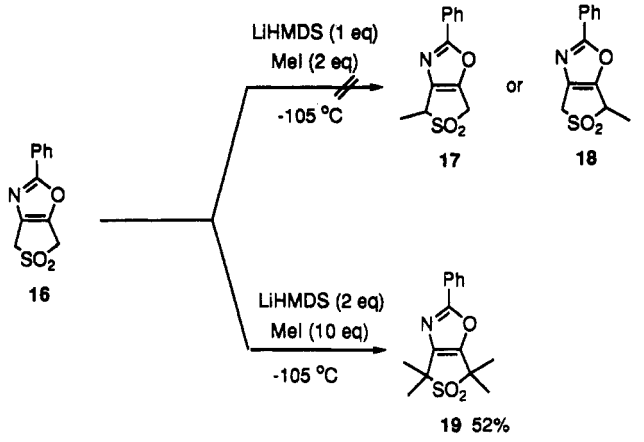
ratio of PCl_5:11a	temp	time	products and yields
4	rt	12 h	**12a** (66%)
4	reflux	1 h	**12a** (72%)
2.5	rt	2 h	**12a** (8%) + **16** (48%)
1	rt	1 h	**16** (68%)

quinodimethane **13** was indeed formed as a transient intermediate. In another test, cycloadduct **15** was obtained in 21% yield when **12a** was treated with Zn and dimethyl fumarate in *tert*-butyl alcohol. However, these yields were not attractive for synthesis.

Careful study of the reaction of **11a** and PCl_5 revealed that desired 3-sulfolene **16** could be obtained as long as the molar ratio of the reactantas, the reaction time, and the reaction temperature were properly controlled (Table 1). Long reaction time and high temperature brought about the formation of dichlorides **12a**. Apparently, desired 3-sulfolene **16** was formed initially (1 h at room temperature) and was gradually converted to **12a** as the reaction continued. The results suggest that under the reaction conditions 3-sulfolene **16** loses SO_2 and undergoes further reaction with PCl_5 to give **12a**. Several experiments indicate that *o*-quinodimethane **13** was the intermediate. An NMR sample of pure **16** in $CDCl_3$ kept at room temperature for 6 h was found to be essentially converted to head-to-head [4 + 4] dimer **21** of *o*-quinodimethane **13**. In addition, stirring a mixture of **16** and dimethyl fumarate in $CHCl_3$ at room temperature for 1 day gave Diels–Alder cycloadduct **15** in 38% yield.

The loss of SO_2 from **16** also took place when K_2CO_3-pretreated $CHCl_3$ was used and when the reaction was carried out in the dark. Therefore, the possibility that the SO_2 extrusion was initiated by light or a trace of acid can be excluded. Compound **16** also decomposed easily in THF but produced only polymeric materials. In the presence of dimethyl fumarate, [4 + 2] cycloadduct **15** was formed in low yield (18%). The ease of SO_2 extrusion at room temperature is unique to **16**; much higher temperatures are required for other known heteroaromatic-

Scheme 4

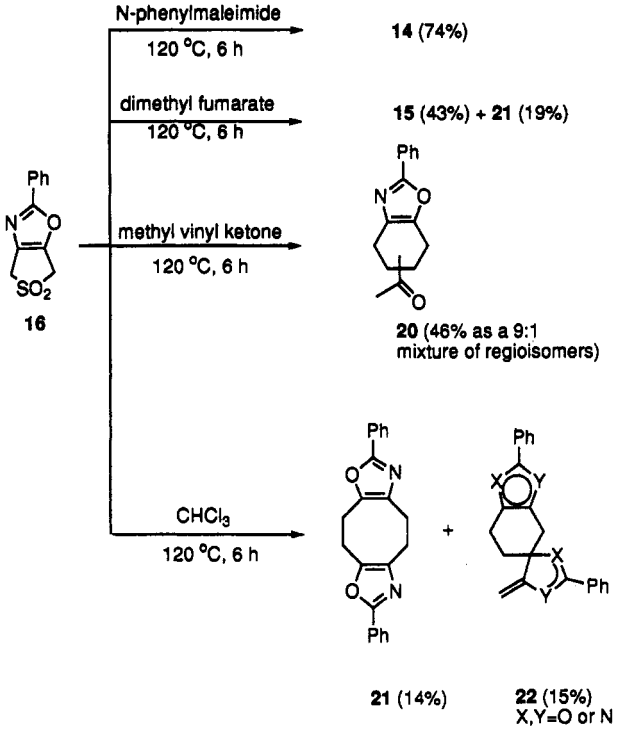


fused 3-sulfolenes to lose SO_2. We do not have a good explanation for this observation yet. Nevertheless, it should be noted that compound **16** could be stored at −20 °C in solution or in pure form for more than 3 months without any appreciable decomposition.

When **16** was treated with an excess of lithium hexamethyldisilazide (LiHMDS) and MeI at −105 °C,[3] tetramethylated product **19** was obtained in 52% yield (Scheme 4). Compound **19** is much more thermally stable than **16**; it does not decompose in refluxing $CHCl_3$.[11] Reaction of **16** with 1 equiv of LiHMDS and MeI gave a complex mixture containing a small amount of recovered starting material but none of monomethylated product **17** or **18**. Since either **17** or **18** should be an intermediate leading to tetramethylated product **19**, we suspect that the monomethylated compound is not stable enough to observe.

Although it gradually decomposes at room temperature, compound **16** serves as a good precursor for *o*-quinodimethane **13**. When **16** was treated with a dienophile in a sealed tube at 120 °C, the Diels–Alder cycloadduct was obtained (Scheme 5). Thermolysis of **16** in the absence of a dienophile afforded head-to-head [4 + 4] dimer **21** in 14% yield. In addition, [4 + 2] dimer **22** was collected in 15% yield, but the structure was not determined. Neither the head-to-tail [4 + 4] dimer nor any of the other three possible [4 + 2] dimers were observed. In conclusion, the success of the SO_2 extrusion of **16** and the subsequent Diels–Alder reactions with dienophiles once again illustrate the broad applicability of heteroaromatic-fused 3-sulfolenes as precursors for heteroaromatic *o*-quinodimethanes.

Scheme 5



Experimental Section

Preparation of 11a–d from 8 via 9a–d. To a suspension of amino alcohol **8** (2.14 g, 14.2 mmol) in CH_2Cl_2 (120 mL) at 0 °C under N_2 was added an acyl chloride (28.3 mmol) dropwise. After the mixture was stirred at 0 °C for 30 min, Et_3N (56.6 mmol) was added; the resulting mixture was warmed to rt gradually, and the stirring was continued for 12 h. The mixture was concentrated under reduced pressure. The crude solid was washed with H_2O (20 mL × 2), Et_2O (40 mL × 2), and MeOH (10 mL) to give essentially pure **9a–e**. Although purification at this stage was not necessary for the preparation of compounds **11**, analytical samples of **9a,c,e** were obtained for confirmation of structures.

3-Benzamido-4-(benzoyloxy)tetrahydrothiophene 1,1-Dioxide (9a): white solid; mp 234–235 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 8.09–8.02 (m, 2H), 7.74–7.69 (m, 2H), 7.66–7.60 (m, 1H), 7.60–7.49 (m, 5H), 6.83 (d, J = 7.0 Hz, 1H), 5.94–5.88 (m, 1H), 5.36–5.22 (m, 1H), 3.82 (dd, J = 13.0, 7.3 Hz, 1H), 3.66 (dd, J = 14.7, 5.1 Hz, 1H), 3.55 (dd, J = 14.7, 2.9 Hz, 1H), 3.37 (dd, J = 13.0, 9.9 Hz, 1H); IR (KBr) 3370, 1724, 1638, 1290, 1118 cm^{-1}; MS (EI) m/z 295 (M^+ − 64), 173, 147, 105 (100), 77. Anal. Calcd for $C_{18}H_{17}NO_5S$: C, 60.16; H, 4.77; N, 3.90. Found: C, 60.15; H, 4.49; N, 3.57.

3-(Cyclohexylcarbamido)-4-[(cyclohexylcarbonyl)oxy]-tetrahydrothiophene 1,1-Dioxide (9c). Two isomers were isolated. The less-polar isomer: white solid; mp 181.5–182 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 6.23 (d, J = 7.8 Hz, 1H), 5.42–5.34 (m, 1H), 4.81–4.71 (m, 1H), 3.67–3.52 (m, 2H), 3.21–3.05 (m, 2H), 2.45–2.28 (m, 1H), 2.19–2.02 (m, 1H), 2.00–1.62 (m, 10H), 1.58–1.13 (m, 10H); IR (KBr) 3274, 2931, 1728, 1634, 1316, 1125 cm^{-1}; MS (EI) m/z 371 (M^+), 264, 196, 153, 125, 83 (100). Anal. Calcd for $C_{18}H_{29}NO_5S$: C, 58.20; H, 7.87; N, 3.77. Found: C, 58.29; H, 7.96; N, 3.65. The more-polar isomer: white solid; mp 212–213 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 5.89 (d, J = 8.1 Hz, 1H), 5.48–5.43 (m, 1H), 3.58 (dd, J = 12.8, 7.4 Hz, 1H), 3.47 (dd, J = 14.7, 5.3 Hz, 1H), 3.35 (dd, J = 14.7, 2.5 Hz, 1H), 3.13 (dd, J = 12.8, 10.2 Hz, 1H), 2.48–2.32 (m, 1H), 2.18–2.01 (m, 1H), 2.00–1.58 (m, 10H), 1.58–1.15 (m, 10H); IR (KBr) 3370, 2928, 1720, 1644, 1304, 1122 cm^{-1}; MS (EI) m/z 371 (M^+), 196, 188, 153, 125, 111, 83 (100). Anal. Calcd for $C_{18}H_{29}NO_5S$: C, 58.20; H, 7.87; N, 3.77. Found: C, 58.16; H, 8.12; N, 3.69.

3-(2,2-Dimethylpropionamido)-4-[(2,2-dimethylpropionyl)oxy]tetrahydrothiophene 1,1-Dioxide (9e). Two isomers were isolated. The less-polar isomer: white solid; mp 203–204 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 6.48 (d, J = 7.0 Hz, 1H), 5.44–5.36 (m, 1H), 4.79–4.68 (m, 1H), 3.70–3.53 (m, 2H), 3.22–3.07 (m, 2H), 1.22 (s, 9H), 1.19 (s, 9H); IR (KBr) 3355, 2968, 1724, 1636, 1319, 1129 cm^{-1}; MS (EI) m/z 320 (M + 1), 319 (M^+), 276, 170 (100), 127. Anal. Calcd for $C_{14}H_{25}NO_5S$: C, 52.64; H, 7.89; N, 4.38. Found: C, 52.64; H, 8.15; N, 4.29. The more-polar isomer: white solid; mp 204.5–205.5 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 6.11 (d, J = 7.5 Hz, 1H), 5.48–5.43 (m, 1H), 5.04–4.89 (m, 1H), 3.65 (dd, J = 12.8, 7.5 Hz, 1H), 3.48 (dd, J = 14.7, 5.0 Hz, 1H), 3.35 (dd, J = 14.7, 2.4 Hz, 1H), 3.10 (dd, J = 12.8, 10.5 Hz, 1H), 1.27 (s, 9H), 1.19 (s, 9H); IR (KBr) 3416, 2961, 1710, 1651, 1284, 1124 cm^{-1}; MS (EI) m/z 320 (M + 1), 212, 170, 127 (100), 85. Anal. Calcd for $C_{14}H_{25}NO_5S$: C, 52.64; H, 7.89; N, 4.38. Found: C, 52.42; H, 8.06; N, 4.20.

A solution of **9a–d** (8.8 mmol) and $NaHCO_3$ (8.8 mmol) in MeOH (500 mL) was stirred at rt for 12 h. The mixture was cooled to 0 °C, and then HCl (37%, 1 mL) was added. The solvent was evaporated under reduced pressure, and acetone (550

mL) was added to crude intermediate **10**. Jones' reagent (prepared from CrO_3, 58.6 mmol; concd H_2SO_4, 4.85 mL; H_2O, 8.79 g) was then added dropwise at 10–15 °C over a period of 4 h, and the mixture was stirred for another 2 h. 2-Propanol (7 mL) was then added dropwise at 0 °C, and the resulting mixture was warmed to rt and stirred for 12 h. The solid was removed by filtration, and the filtrate was concentrated under reduced pressure. Ethyl acetate (500 mL) was added, and the solution was dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by column chromatography [silica gel, EtOAc/hexane (9:1)] to give **11**. The yields of the products are listed in Scheme 2.

3-Benzamido-4-oxotetrahydrothiophene 1,1-Dioxide (11a): white solid; mp 184.5–185 °C; ^{1}H NMR (200 MHz, acetone-d_6) δ 8.75 (s, 1H), 7.96–7.88 (m, 2H), 7.64–7.43 (m, 3H), 4.96–4.80 (m, 1H), 4.39–3.90 (m, 4H); IR (KBr) 3433, 1757, 1649, 1316, 1117 cm^{-1}; MS (EI) *m/z* 189 (M^+ – 64), 105 (100), 77. Anal. Calcd for $C_{11}H_{11}NO_4S$: C, 52.16; H, 4.38; N, 5.53. Found: C, 52.13; H, 4.55; N, 5.33.

3-Acetamido-4-oxotetrahydrothiophene 1,1-Dioxide (11b): white solid; mp 167–168 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.31 (br s, 1 H), 4.69–4.45 (m, 1H), 4.10 (d, J = 17.0 Hz, 1H), 3.90–3.68 (m, 3H), 2.07 (s, 3H); IR (KBr) 3261, 1757, 1634, 1311, 1122 cm^{-1}; MS (EI) *m/z* 133 (M^+ – 58), 119, 97, 83, 69 (100). Anal. Calcd for $C_9H_9NO_4S$: C, 37.69; H, 4.74; N, 7.33. Found: C, 37.75; H, 4.80; N, 7.26.

3-(Cyclohexanecarboxamido)-4-oxotetrahydrothiophene 1,1-Dioxide (11c): white solid; mp 167–168.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.31 (d, J = 5.7 Hz, 1H), 4.54–4.40 (m, 1H), 4.14 (d, J = 17.6 Hz, 1H), 3.88–3.72 (m, 3H), 2.25–2.08 (m, 1H), 1.93–1.61 (m, 5H), 1.51–1.15 (m, 5H); IR (KBr) 3308, 2930, 1753, 1629, 1319, 1125 cm^{-1}; MS (EI) *m/z* 197 (M^+ – 62), 128, 83 (100), 72. Anal. Calcd for $C_{11}H_{17}NO_4S$: C, 50.95; H, 6.61; N, 5.40. Found: C, 50.91; H, 6.68; N, 5.24.

3-(*p*-Nitrobenzamido)-4-oxotetrahydrothiophene 1,1-Dioxide (11d): white solid; mp 198–200 °C; ^{1}H NMR (200 MHz, acetone-d_6) δ 9.05 (br s, 1H), 8.38–8.30 (m, 2H), 8.18–8.11 (m, 2H), 5.08–4.92 (m, 1H), 4.28–3.85 (m, 4H); IR (KBr) 3435, 1759, 1654, 1319, 1125 cm^{-1}; MS (EI) *m/z* 234 (M^+ – 62), 150 (100), 120, 104; HRMS calcd for $C_{11}H_{10}N_2O_6S$ 298.0260, found 298.0257. The ^{1}H NMR spectra revealed the purity of the product **11d** to be better than 95%.

Preparation of 12a–c from 11a–c. A solution of compound **11** (0.31 mmol) and PCl_5 (0.77 mmol) in $CHCl_3$ (10 mL) was refluxed under N_2 for 1 h. The mixture was cooled to rt and ice (3 g) was added. The mixture was diluted with CH_2Cl_2 (30 mL) and washed with saturated aqueous $NaHCO_3$ (10 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by HPLC [LiChrosorb™ column, EtOAc/hexane (1:1)] to give **12**. The yields are listed in Scheme 3.

4,5-Bis(chloromethyl)-2-phenyloxazole (12a): yellow solid; mp 100–101 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.12–8.02 (m, 2H), 7.54–7.43 (m, 3H), 4.75 (s, 2H), 4.60 (s, 2H); IR (KBr) 1422, 1357, 1232, 773, 685 cm^{-1}; MS (EI) *m/z* 243 (M^+ + 2), 241 (M^+), 206, 122, 105 (100), 77; HRMS calcd for $C_{11}H_9Cl_2NO$ 241.0061, found 241.0077. The ^{1}H NMR spectra revealed the purity of product **12a** to be better than 95%.

4,5-Bis(chloromethyl)-2-methyloxazole (12b): yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.62 (s, 2H), 4.49 (s, 2H), 2.48 (s, 3H); IR (neat) 1686, 1575, 1430, 1348, 1261, 1230, 1130, 808, 705 cm^{-1}; MS (EI) *m/z* 181 (M^+ + 2), 179 (M^+), 146, 144 (100); HRMS calcd for $C_6H_7Cl_2NO$ 178.9905, found 178.9916. The ^{1}H NMR spectra revealed the purity of product **12b** to be better than 95%.

4,5-Bis(chloromethyl)-2-cyclohexyloxazole (12c): colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.63 (s, 2H), 4.50 (s, 2H), 2.78 (tt, J = 11.3, 3.7 Hz, 1H), 2.06 (dd, J = 13.6, 2.2 Hz, 2H), 1.85–1.79 (m, 2H), 1.73–1.50 (m, 4H), 1.45–1.25 (m, 2H); IR (neat) 2934, 1566, 1440, 1348, 1261, 1132, 695 cm^{-1}; MS (EI) *m/z* 249 (M^+ + 2), 212 (M^+, 100), 179, 130, 83; HRMS calcd for $C_{11}H_{15}Cl_2NO$ 247.0532, found 247.0539. The ^{1}H NMR spectra revealed the purity of product **12c** to be better than 95%.

2-Phenyl-4,6-dihydrothieno[3,4-*d*]oxazole 5,5-Dioxide (16). To a solution of sulfone **11a** (58.2 mg, 0.23 mmol) in $CHCl_3$ (10 mL) at 0 °C under N_2 was added PCl_5 (57.5 mg, 0.27 mmol), and the mixture was stirred at rt for 1 h. The mixture was diluted with CH_2Cl_2 (50 mL) and washed with saturated aqueous $NaHCO_3$ (20 mL × 3). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by HPLC [LiChrosorb column, EtOAc/hexane (1:1)] to give **16** (36.8 mg, 68%): white solid; mp 109 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.06–8.00 (m, 2H), 7.52–7.26 (m, 3H), 4.44 (t, J = 1.1 Hz, 2H), 4.36 (t, J = 1.1 Hz, 2H); IR (KBr) 1306, 1102 cm^{-1}; MS (EI) *m/z* 235 (M^+), 171 (100); HRMS calcd for $C_{11}H_9NOS$ 235.0304, found 235.0309. The ^{1}H NMR spectra revealed the purity of product **16** to be better than 95%.

4,4,6,6-Tetramethyl-2-phenyl-4,6-dihydrothieno[3,4-*d*]oxazole 5,5-Dioxide (19). To a solution of sulfone **16** (38.2 mg, 0.16 mmol), HMPA (0.2 mL, 1.2 mmol), and MeI (0.1 mL, 1.6 mmol) in anhyd THF (5 mL) at −105 °C under N_2 was added LiHMDS [prepared from 1.3 M n-BuLi (0.6 mL) and 1,1,1,3,3,3-hexamethyldisilazane (0.19 mL)] dropwise. After the mixture was stirred for 30 min at −55 °C, H_2O (2 mL) was added in one portion, and the resulting mixture was warmed to rt gradually. The mixture was concentrated under reduced pressure. The residue was eluted with EtOAc/hexane (1:1) through a silica gel column to remove HMPA and then purified by HPLC [LiChrosorb column, EtOAc/hexane (1:1)] to give **18** (24.7 mg, 52%): light orange oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.07–8.02 (m, 2H), 7.50–7.27 (m, 3H), 1.71 (m, 12H); IR (neat) 1306, 1094 cm^{-1}; MS (EI) *m/z* 298 (M^+), 227 (100), 212, 131, 105, 77; HRMS calcd for $C_{15}H_{17}NO_3S$ 291.0930, found 291.0931. The ^{1}H NMR spectra revealed the purity of product **19** to be better than 95%.

7,8a-Dihydro-2,6-diphenyl-*cis*-4*H*-oxazolo[4,5-*f*]isoindole-5,7(4a*H*,6*H*)-dione (14). A solution of sulfone **16** (8.5 mg, 0.036 mmol) and *N*-phenylmaleimide (12.5 mg, 0.072 mmol) in $CHCl_3$ (3 mL) was heated at 120 °C in a sealed tube under N_2 for 6 h. The solvent was evaporated under reduced pressure, and the residue was purified by HPLC (LiChrosorb column, EtOAc/hexane (1:1)) to give **14** (9.2 mg, 74%): white solid; mp 167–168 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.02–7.96 (m, 2H), 7.51–7.34 (m, 6H), 7.30–7.25 (m, 2H), 3.64–3.16 (m, 6H); IR (KBr) 3070, 1679 cm^{-1}; MS (EI) *m/z* 344 (M^+), 149, 121, 105 (100), 77. Anal. Calcd for $C_{21}H_{16}N_2O_3$: C, 73.24; H, 4.68; N, 8.13. Found: C, 72.94; H, 4.72; N, 7.83.

5,6-Bis(methoxycarbonyl)-*trans*-4,5,6,7-tetrahydrobenzo[*d*]oxazole (15). A solution of sulfone **16** (12.2 mg, 0.05 mmol) and dimethyl fumarate (18.7 mg, 0.13 mmol) in $CHCl_3$ (3 mL) was heated at 120 °C in a sealed tube under N_2 for 6 h. The solvent was evaporated under reduced pressure, and the residue was purified by HPLC [LiChrosorb column, EtOAc/hexane (3:1)] to give **15** (7 mg, 43%) and **21** (3.3 mg, 19%). Compound **15**: white solid; mp 112–113 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.01–7.94 (m, 2H), 7.47–7.40 (m, 3H), 3.75 (s, 3H), 3.74 (s, 3H), 3.38–2.81 (m, 6H); IR (KBr) 1724, 1168, 688 cm^{-1}; MS (EI) *m/z* 315 (M^+, 100), 284, 256, 196; HRMS calcd for $C_{17}H_{17}NO_5$ 315.1107, found 315.1109. The ^{1}H NMR spectra revealed the purity of product **15** to be better than 95%.

5-Acetyl-4,5,6,7-tetrahydrobenzo[*d*]oxazole (20). A solution of sulfone **16** (12.2 mg, 0.05 mmol) and methyl vinyl ketone (0.01 mL, 0.12 mmol) in $CHCl_3$ (3 mL) was heated at 120 °C in a sealed tube under N_2 for 6 h. The solvent was evaporated under reduced pressure, and the residue was purified by HPLC [LiChrosorb column, EtOAc/hexane (1:1)] to give **20** [5.8 mg, 46% as a 1:9 mixture of unidentified regioisomers]. The minor isomer: white solid; mp 72–73 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.01–7.97 (m, 2H), 7.45–7.41 (m, 3H), 2.95–2.70 (m, 5H), 2.27 (s, 3H), 2.28–2.21 (m, 1H), 2.07–1.82 (m, 1H); IR (KBr) 2922, 1683, 691, 602 cm^{-1}; MS (EI) *m/z* 241 (M^+), 198 (100), 84; HRMS calcd for $C_{15}H_{15}NO_2$ 241.1104, found 241.1099. The ^{1}H NMR spectra revealed the purity of the product to be better than 95%. The major isomer: white solid; mp 36–37 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.02–7.97 (m, 2H), 7.47–7.41 (m, 3H), 3.05–2.83 (m, 3H), 2.73–2.67 (m, 2H), 2.29 (s, 3H), 2.29–2.24 (m, 1H), 2.00–1.70 (m, 1H); IR (KBr) 2939, 1693, 709, 691 cm^{-1}; MS (EI) *m/z* 241 (M^+), 198, 84 (100); HRMS calcd for $C_{15}H_{15}NO_2$ 241.1104, found 241.1091. The ^{1}H NMR spectra revealed the purity of the product to be better than 95%.

Dimerization of 2-Phenyl-4,6-dihydrothieno[3,4-*d*]oxazole 5,5-Dioxide (16). A solution of sulfone **16** (13.3 mg, 0.056 mmol) in $CHCl_3$ (4 mL) was heated at 120 °C in a sealed tube

under N_2 for 6 h. The solvent was evaporated under reduced pressure, and the residue was purified by HPLC [LiChrosorb column, EtOAc/hexane (1:1)] to give **21** (2.8 mg, 14%) and **22** (2.9 mg, 15%). Compound **21**: white solid; mp 227–228 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.97–7.94 (m, 4H), 7.41–7.39 (m, 6H), 3.23 (s, 4H), 3.09 (s, 4H); IR (KBr) 2914, 709, 685 cm^{-1}; MS (EI) m/z 342 (M^+), 172, 149 (100), 105 (100), 77; HRMS calcd for $C_{22}H_{18}N_2O_2$ 342.1369, found 342.1356. The ^{1}H NMR spectra revealed the purity of product **21** to be better than 95%. Compound **22**: colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04–7.99 (m, 4H), 7.54–7.41 (m, 6H), 4.85 (d, J = 3.0 Hz, 1H), 4.29 (d, J = 3.0 Hz, 1H), 3.12 (d, J = 18 Hz, 1H), 3.00–2.72 (m, 3H), 2.16–2.11 (m, 1H), 2.05–1.92 (m, 1H); IR (KBr) 1646, 1089, 1060 cm^{-1}; MS (EI) m/z 342 (M^+), 149 (100), 103; HRMS calcd for $C_{22}H_{18}N_2O_2$ 342.1369, found 342.1364. The ^{1}H NMR spectra revealed the purity of product **22** to be better than 95%.

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Supplementary Material Available: Copies of ^{1}H NMR spectra of **11d**, **12a–c**, **15**, **16**, and **19–22** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.