Notes

A Novel Route to the Preparation of Pyrazole Analogues of *o*-Xylylene

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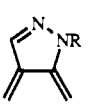
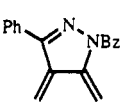
The use of *o*-xylylene (*o*-quinodimethane) in the synthesis of natural products has been extensively explored.[1] On the other hand, the study of heterocyclic *o*-xylylenes has just started to draw attention. Recently, there has been an increasing number of reports on the generation and reactivity of some heterocyclic *o*-xylylenes containing one[2], two,[3] or three[4] heteroatoms.

The generation of the pyrazole *o*-xylylene 1 was first tried by Storr et al.[3a] who attempted to use the technique of flash vacuum pyrolysis to convert (1-phenyl-5-methylpyrazol-4-yl)methyl 4-chlorobenzoate to the *o*-xylylene **1b**. Unfortunately, there was no evidence for the formation of **1b** since the cocondensation of the pyrolysate with PhSH, HCl, or SO_2 failed to give the anticipated adduct. Stephanidou-Stephanatou[3b] showed that, by dehalogenation of 1-benzoyl-3-phenyl-4,5-bis(bromomethyl)pyrazole, the *o*-xylylene **2** could be generated and reacted with a number of dienophiles in fair yields. However, the generality of this approach was not discussed. More recently, Storr[5] reported a concise route to the parent pyrazole *o*-xylylene **1a** via the corresponding 3-sulfolene **3**, albeit in low yield. Precursors for N-substituted pyrazole *o*-xylylenes **1**, which lead to the corresponding *o*-xylylenes in better yield, could be prepared by the N-substitution reactions of **3**. However, unseparable mixtures of N1- and N2-substituted pyrazole-fused 3-sulfolenes were obtained. Consequently, the Diels–Alder reactions of dienophiles with the *o*-xylylenes generated therefrom also gave mixtures of cycloadducts.

We have reported several general approaches to the synthesis of heterocycle-fused 3-sulfolenes as precursors for the corresponding *o*-xylylenes and demonstrated the potential applications in organic synthesis.[6] We now report that the readily available compound **4**,[7] which contains a masked 1,3-dicarbonyl functionality, is a useful intermediate for the preparation of pyrazole *o*-xylylenes.



1a R = H
1b R = Ph



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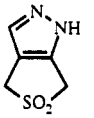

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When compound **4** was treated with hydrazine hydrate (10 equiv) followed by acid-induced deprotection of the acetal **5** which was not isolated, sequential cyclization and dehydration reactions took place spontaneously and the bicyclic heterocycle **6** was produced in 61% yield (Scheme I). Subsequent oxidation of **6** with *m*-chloroperbenzoic acid (*m*-CPBA) afforded **3** in quantitative yield. Alternatively, compound **3** could be prepared in better total yield from **4** by reacting it with *t*-BocNHNH$_2$ (1.1 equiv) instead of NH_2NH_3OH. Hydrolytic removal of the *t*-Boc group, deprotection of the acetal of **7**, and the formation of the pyrazole ring could be achieved simultaneously with 20% v/v H_2SO_4.

In principle, this strategy could be readily extended for the preparation of N-substituted derivatives of **3** (Scheme II). Thus, when **4** and phenylhydrazine were reacted, a 10:1 mixture of the pyrazoles **8** and **9** was obtained. The regioselectivity indicates that the unsubstituted nitrogen atom of phenylhydrazine is the main reaction site with the aldehyde functionality of **4**. Oxidation of **8** and **9** with *m*-CPBA produced the corresponding 3-sulfolenes **10** and **11**, respectively. It was thought that by introducing a stronger electron-withdrawing group on the reacting hydrazine, the regioselectivity of this reaction should be enhanced. Indeed, when 2,4-dinitrophenylhydrazine was subject to the reaction sequence, compound **12** was produced as the only product (Scheme II). The synthetic approach shown in these two schemes illustrates a general method for the preparation of the parent and substituted pyrazole-fused 3-sulfolenes.

It has been well-established that 3-sulfolenes can be conveniently deprotonated and alkylated to give the α-substituted derivatives.[8] This methodology should be applicable to the pyrazole-fused 3-sulfolenes for the preparation of their derivatives. Treatment of **10** with lithium hexamethyldisilazide (LiHMDS, 1.1 equiv) and methyl iodide (10 equiv) at −105 °C smoothly produced the methylated product **13** in 66% yield. When 2 equiv of base was used, α,α-dimethylated product **14** was obtained (Scheme III) without the formation of any α,α'-dimethylated product. A NOESY experiment on **14** revealed that the carbon bearing the two methyl groups

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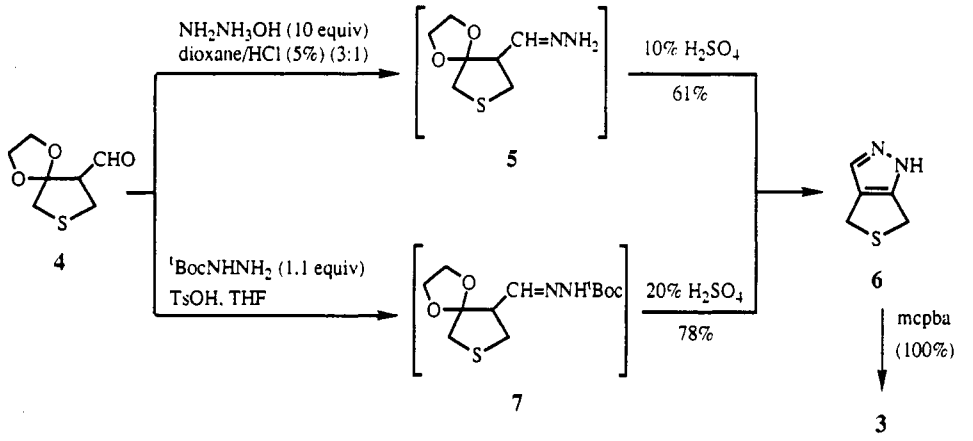
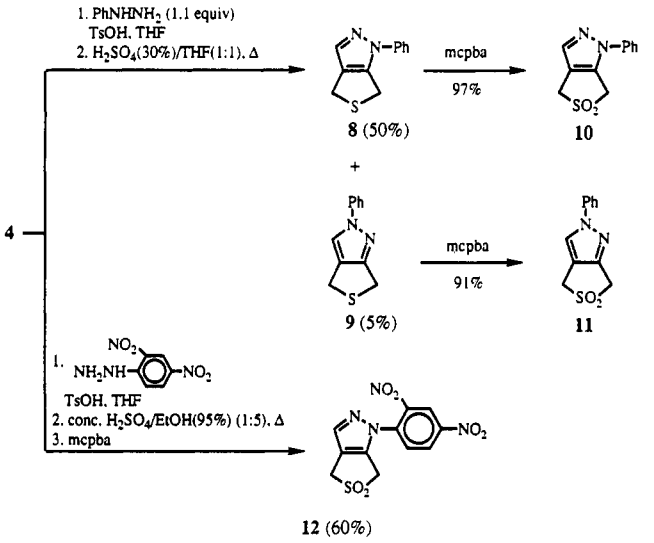
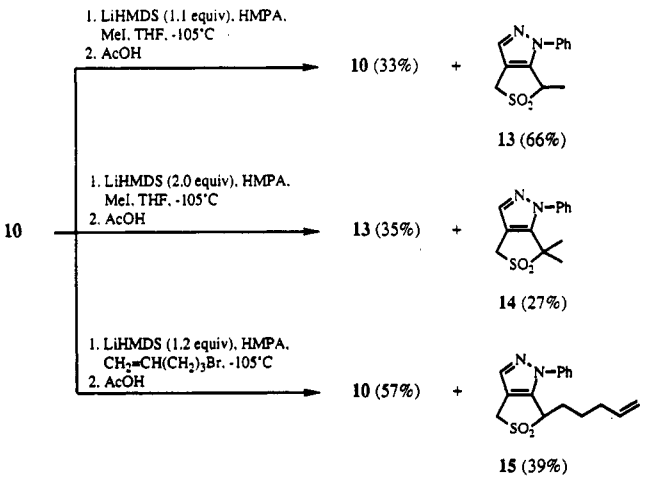
Scheme I



Scheme II

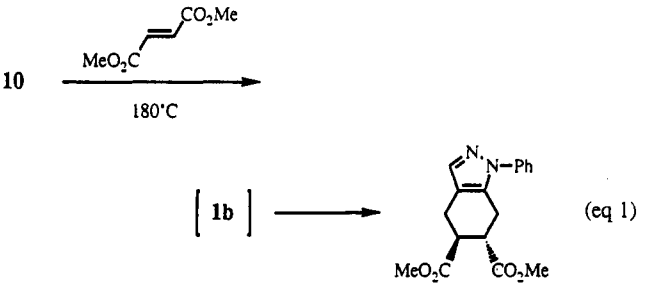


Scheme III

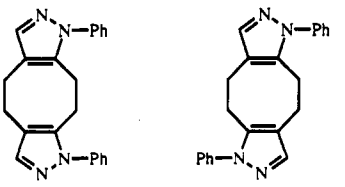


is on the same side of the *N*-phenyl group. Accordingly, the structural assignment of **13**, from which **14** was produced, should also be correct. Under similar reaction conditions, compound **15** was prepared from the reaction of **10** and 5-bromo-1-pentene. However, attempted deprotonation/substitution reactions of the parent compound **3** resulted in the formation of complex mixtures.

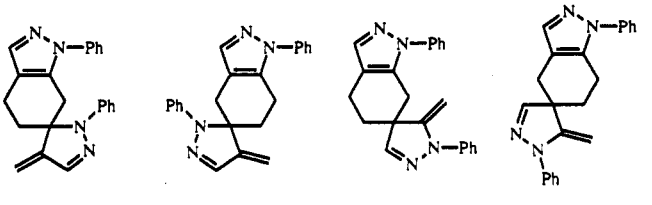
Heating compound **10** with dimethyl fumarate at 180 °C in a sealed tube for 20 min readily produced the [4 + 2] cycloadduct **16**, presumably via the *o*-xylylene **1b** (eq 1). The excellent yield of this reaction (97%) indicates that both the extrusion reaction of SO_2 from **10** and the cycloaddition reaction of **1b** with dimethyl fumarate are extremely high-yielding. Thus, compound **10** serves as an ideal precursor for the *o*-xylylene **1b**. On the other hand, attempts to trap the parent *o*-xylylene **1a** by the thermolysis of **3** were futile because only tarry material was produced.



In the absence of a dienophile, the highly reactive intermediate **1b** thus generated dimerizes to give a mixture of the head-to-head [4 + 4] dimer **17** (12%), the head-to-tail [4 + 4] dimer **18** (6%), and all of the four possible [4 + 2] dimers **19–22** (3% altogether). The four [4 + 2] dimers could not be separated. The low overall yield (21%) of the dimers might be due to the rapid polymerization of **1b**. Nevertheless, this is the first time that the dimerization of a pyrazole *o*-xylylene could be observed.

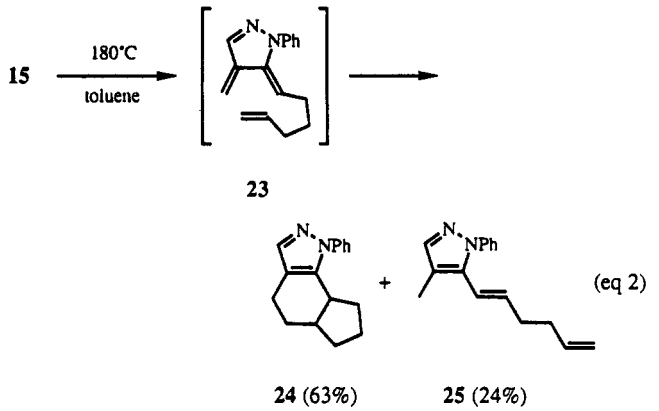


17 18



19 20 21 22

When compound **15** was heated at 180 °C for 30 min, an intramolecular Diels–Alder reaction of the intermediate *o*-xylylene **23** took place to produce the tricyclic pyrazole compound **24** (63%) (eq 2). This reaction provides a



convenient route to the synthesis of multicyclic pyrazoles. The side product **25** should have been formed from **23** via a thermally allowed [1,5] hydrogen shift process. Although the extrusion of SO_2 from the pyrazole-fused 3-sulfolenes **10** and **15** proceeded smoothly (within 30 min) at 180 °C, the isomeric compound **11** remained intact upon heating at this temperature for more than 90 min.

In summary, we have synthesized a series of pyrazole-fused 3-sulfolenes and performed the deprotonation/alkylation reactions at the α-position of the 3-sulfolene ring. We have also thermolyzed these pyrazole-fused 3-sulfolenes to the corresponding *o*-xylylenes and trapped them by inter- and intramolecular Diels–Alder reactions. These reactions illustrate the usefulness of pyrazole *o*-xylylenes in organic synthesis.

Experimental Section

4,6-Dihydrothieno[3,4-*c*]pyrazole (6). Method A. To NH_2-NH_3OH (10 mL) at 0 °C was added a solution of the aldehyde **4** (750 mg, 4.30 mmol) in dioxane (3.0 mL) dropwise. The mixture was stirred for 10 min, at which time 5% v/v HCl (1.0 mL) was added, and the stirring was continued for another 4 h at room temperature. The mixture was neutralized with saturated aqueous $NaHCO_3$ and extracted with EtOAc (30 mL × 2). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. To the residue was added 10% v/v H_2SO_4 (10 mL), and stirring was continued at room temperature for 10 h. The mixture was neutralized with saturated aqueous $NaHCO_3$ and then extracted with EtOAc (30 mL × 3). The organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, EtOAc/hexane (1:1)) to give **6** (331 mg, 2.62 mmol, 61%).

Method B. A mixture of $H_2NNHBoc$ (160 mg, 1.21 mmol), $TsOH·H_2O$ (catalytic amount), and the aldehyde **4** (191 mg, 1.10 mmol) in THF (4.0 mL) was stirred at room temperature for 4 h, at which time 20% v/v H_2SO_4 (4.0 mL) was added, and stirring was continued for another 10 h at room temperature. The mixture was neutralized with saturated aqueous $NaHCO_3$ and then extracted with EtOAc (30 mL × 3). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by HPLC (LiChrosorb column, EtOAc/hexane (3:1)) to give **6** (108 mg, 0.856 mmol, 78%): white solid; mp 132–133 °C; ^1H NMR ($CDCl_3$) δ 8.32 (bs, 1 H), 7.25 (s, 1 H), 4.00 (s, 2 H), 3.93 (s, 2 H); IR (KBr) 3149, 2903, 1373, 1159, 809 cm^{-1}; MS (EI) *m/z* 126 (M^+, 100), 111, 97, 81. Anal. Calcd for $C_5H_6N_2S$: C, 47.59; H, 4.79; N, 22.20. Found: C, 47.73; H, 4.78; N, 22.16.

4,6-Dihydrothieno[3,4-*c*]pyrazole 5,5-Dioxide (3). To a solution of the sulfide **6** (90.2 mg, 0.715 mmol) in CH_2Cl_2 (5.0 mL) at 0 °C was added *m*-CPBA (55%, 670 mg, 2.14 mmol), and the mixture was stirred at room temperature for 20 min. The crude mixture was concentrated under reduced pressure, and the THF-soluble portion was purified by preparative thin-layer chromatography (silica gel, EtOAc/hexane (3:1)) to give **3** (113 mg, 0.714 mmol, 100%): white solid; mp 156–157 °C; ^1H NMR (DMSO-d_6) δ 13.11 (bs, 1 H), 7.79 (bs, 1 H), 4.32 (s, 2 H), 4.28 (s, 2 H); IR (KBr) 3352, 1295, 1086 cm^{-1}; MS (EI) *m/z* 158 (M^+), 94, 72 (100). The spectroscopic data are identical with the literature.[5]

1-Phenyl-4,6-dihydrothieno[3,4-*c*]pyrazole (8) and 2-Phenyl-4,6-dihydrothieno[3,4-*c*]pyrazole (9). A mixture of $PhNHNH_2$ (261 mg, 2.41 mmol), $TsOH·H_2O$ (catalytic amount), and the aldehyde **4** (340 mg, 1.95 mmol) in THF (3.0 mL) was stirred at room temperature for 1 h, at which time 30% v/v H_2SO_4 (3.0 mL) was added, and stirring was continued for 10 h. The mixture was diluted with brine (30 mL) and extracted with EtOAc (30 mL × 3). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by HPLC (LiChrosorb column, EtOAc/hexane (1:2)) to give **8** (196 mg, 0.969 mmol, 50%) and **9** (20.0 mg, 0.0989 mmol, 5%). Compound **8**: white solid; mp 71–72 °C; ^1H NMR ($CDCl_3$) δ 7.57–7.20 (m, 6 H), 4.12 (t, J = 2.7 Hz, 2 H), 3.90 (t, J = 2.7 Hz, 2 H); IR (KBr) 2920, 1593, 1496, 1389, 751 cm^{-1}; MS (EI) *m/z* 202 (M^+, 100), 169, 157. Anal. Calcd for $C_{11}H_{10}N_2S$: C, 65.32; H, 4.98; N, 13.85. Found: C, 65.15; H, 4.57; N, 13.60. Compound **9**: white solid; mp 99–100 °C; ^1H NMR ($CDCl_3$) δ 7.64–7.20 (m, 6 H), 4.08–4.06 (m, 2 H), 3.99–3.97 (m, 2 H); IR (KBr) 2918, 1572, 1369, 952, 751, 679 cm^{-1}; MS (EI) *m/z* 202 (M^+, 100), 169, 157; HRMS calcd for $C_{11}H_{10}N_2S$ 202.0565, found 202.0571. The ^1H NMR spectrum of compound **9** showed its purity to be greater than 95%.

1-Phenyl-4,6-dihydrothieno[3,4-*c*]pyrazole 5,5-Dioxide (10). To a solution of the sulfide **8** (73.2 mg, 0.362 mmol) in CH_2Cl_2 (4.0 mL) at 0 °C was added *m*-CPBA (55%, 251 mg, 0.800 mmol), and the mixture was stirred at room temperature for 20 min. The mixture was diluted with CH_2Cl_2 (40 mL) and washed with saturated aqueous $NaHCO_3$ (30 mL × 3) and saturated aqueous $Na_2S_2O_3$ (30 mL × 3). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by HPLC (LiChrosorb column, EtOAc/hexane (3:1)) to give **10** (82.3 mg, 0.351 mmol, 97%): white solid; mp 154–156 °C; ^1H NMR ($CDCl_3$) δ 7.68 (s, 1 H), 7.50–7.30 (m, 5 H), 4.45 (s, 2 H), 4.32 (s, 2 H); IR (KBr) 1595, 1315, 1120, 754 cm^{-1}; MS (EI) *m/z* 234 (M^+), 170 (100). Anal. Calcd for $C_{11}H_{10}N_2O_2S$: C, 56.06; H, 4.36; N, 11.79. Found: C, 56.40; H, 4.30; N, 11.96.

2-Phenyl-4,6-dihydrothieno[3,4-*c*]pyrazole 5,5-Dioxide (11). To a solution of the sulfide **9** (17.1 mg, 0.0846 mmol) in CH_2Cl_2 (3.0 mL) at 0 °C was added *m*-CPBA (55%, 59.0 mg, 0.188 mmol), and the mixture was stirred at room temperature for 20 min. The mixture was diluted with CH_2Cl_2 (30 mL) and washed with saturated aqueous $NaHCO_3$ (20 mL × 3) and saturated aqueous $Na_2S_2O_3$ (20 mL × 3). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to give **11** (18.1 mg, 0.0773 mmol, 91%): white solid; mp 170–171 °C; ^1H NMR ($CDCl_3$) δ 7.88 (s, 1 H), 7.67–7.30 (m, 5 H), 4.36 (s, 2 H), 4.33 (d, J = 2.3 Hz, 1 H), 4.31 (d, J = 2.3 Hz, 1 H); IR (KBr) 1300, 1099, 755 cm^{-1}; MS (EI) *m/z* 234 (M^+, 100), 170; HRMS calcd for $C_{11}H_{10}N_2O_2S$ 234.0463, found 234.0458. The ^1H NMR spectrum of compound **11** showed its purity to be greater than 95%.

1-(2,4-Dinitrophenyl)-4,6-dihydrothieno[3,4-*c*]pyrazole 5,5-Dioxide (12). A mixture of dinitrophenylhydrazine (140 mg, 0.710 mmol), $TsOH·H_2O$ (catalytic amount), and the aldehyde **4** (111 mg, 0.637 mmol) in 95% EtOH (10 mL) was stirred at room temperature for 6 h, at which time concd H_2SO_4 (2.0 mL) was added, and stirring was continued for another 4 h at 60 °C. The mixture was diluted with brine (40 mL) and extracted with CH_2Cl_2 (40 mL × 3). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (40 mL), *m*-CPBA (55%, 450 mg, 1.43 mmol) was added, and the mixture was stirred at room temperature for 30 min. The mixture was concentrated under reduced pressure, and the crude product was recrystallized (EtOAc/hexane) to give pure product **12** (124 mg, 0.382 mmol, 60%): yellow solid; mp 170 °C dec; ^1H NMR (acetone-d_6) δ 8.86 (d, J = 2.5 Hz, 1 H), 8.69 (dd, J = 8.5, 2.5 Hz, 1 H), 8.20 (d, J

= 8.5 Hz, 1 H), 7.85 (s, 1 H), 4.72 (s, 2 H), 4.43 (s, 2 H); IR (KBr) 3094, 1604, 1327, 1116 cm^{-1}; MS(FAB) m/z 325 ($M^+ + 1$); HRMS-(FAB) calcd for $C_{11}H_8N_4O_6S$ 325.0243 ($M^+ + 1$), found 325.0253. The ^1H NMR spectrum of compound **12** showed its purity to be greater than 95%.

6-Methyl-1-phenyl-4,6-dihydrothieno[3,4-*c*]pyrazole 5,5-Dioxide (13). To a solution of the sulfone **10** (53.0 mg, 0.226 mmol), HMPA (0.20 mL, 1.1 mmol), and MeI (0.10 mL, 1.60 mmol) in dry THF (2.0 mL) at −105 °C under N_2 was added LiHMDS (1.5 M n-BuLi 0.17 mL, HMDS 0.10 mL) dropwise. After the mixture was stirred for 15 min, AcOH (0.10 mL) was added in one portion and the resulting mixture was warmed to room temperature gradually. The mixture was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, EtOAc/hexane (1:1)) to give the mixture of **10** and **13** which could not be separated by HPLC (total 53.9 mg, **10**/**13** (1:2) from NMR integration).

6,6-Dimethyl-1-phenyl-4,6-dihydrothieno[3,4-*c*]pyrazole 5,5-Dioxide (14). To a solution of the sulfone **10** (56.0 mg, 0.239 mmol), HMPA (0.20 mL, 1.1 mmol), and MeI (0.10 mL, 1.60 mmol) in dry THF (2.0 mL) at −105 °C under N_2 was added LiHMDS (1.5 M *n*-BuLi 0.32 mL, HMDS 0.20 mL) dropwise. After the mixture was stirred for 15 min, AcOH (0.10 mL) was added in one portion and the resulting mixture was warmed to room temperature 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 (3:1)) to give **13** (21.0 mg, 0.0846 mmol, 35%) and **14** (17.0 mg, 0.0648 mmol, 27%). Compound **13**: colorless oil; ^1H NMR ($CDCl_3$) δ 7.67 (s, 1 H), 7.52–7.35 (m, 5 H), 4.51 (q, J = 7.1 Hz, 1 H), 4.35 (d, J = 14.2 Hz, 1 H), 4.24 (d, J = 14.2 Hz, 1 H), 1.42 (d, J = 7.1 Hz, 3 H); IR (film) 2983, 1595, 1501, 1401, 1314, 1187, 1121, 990, 759 cm^{-1}; MS (EI) m/z 248 (M^+), 184, 83 (100); HRMS calcd for $C_{12}H_{12}N_2O_2S$ 248.0619, found 248.0611. The ^1H NMR spectrum of compound **13** showed that it contained 5% of compound **10**. Compound **14**: white solid; mp 208–209 °C; ^1H NMR ($CDCl_3$) δ 7.64 (s, 1 H), 7.60–7.39 (m, 5 H), 4.25 (s, 2 H), 1.51 (s, 6 H); IR (KBr) 2980, 1300, 1098, 753 cm^{-1}; MS (EI) m/z 262 (M^+), 198 (100), 183; HRMS calcd for $C_{13}H_{14}N_2O_2S$ 262.0688, found 262.0773. The ^1H NMR spectrum of compound **14** showed its purity to be greater than 95%.

6-(4-Pentenyl)-1-phenyl-4,6-dihydrothieno[3,4-*c*]pyrazole 5,5-Dioxide (15). To a solution of the sulfone **10** (53.5 mg, 0.228 mmol), HMPA (0.20 mL, 1.1 mmol), and 5-bromo-1-pentene (0.10 mL, 0.84 mmol) in dry THF (1.0 mL) at −105 °C under N_2 was added LiHMDS (1.5 M *n*-BuLi 0.18 mL, HMDS 0.10 mL) dropwise, and the resulting solution was warmed to −78 °C. After the mixture was stirred for 30 min at −78 °C, AcOH (0.10 mL) was added and the resulting mixture was warmed to room temperature 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 (3:2)) to give **10** (31.0 mg, 0.132 mmol, 57%) and **15** (27.0 mg, 0.0893 mmol, 39%). Compound **15**: white solid; mp 96–97 °C; ^1H NMR ($CDCl_3$) δ 7.67 (s, 1 H), 7.52–7.35 (m, 5 H), 5.70–5.45 (m, 1 H), 4.95–4.80 (m, 2 H), 4.46 (q, J = 4.3 Hz, 1 H), 4.33 (d, J = 14.2 Hz, 1 H), 4.20 (d, J = 14.2 Hz, 1 H), 2.50–1.70 (m, 2 H), 1.50–1.30 (m, 2 H); IR (KBr) 2936, 1597, 1502, 1322, 1119, 987, 756 cm^{-1}; MS (EI) m/z 238 ($M^+ - SO_2$), 209, 197 (100), 183, 170; HRMS calcd for $C_{16}H_{18}N_2O_2S$ 302.1089, found 302.1099. The ^1H NMR spectrum of compound **15** reveals its purity to be greater than 95%.

5,6-Bis(methoxycarbonyl)-*trans*-4,5,6,7-tetrahydrobenzo[*c*]pyrazole (16). A solution of the sulfone **10** (27.1 mg, 0.116 mmol) and dimethyl fumarate (20 mg, 0.14 mmol) in $CHCl_3$ (2.0 mL) was heated at 180 °C in a sealed tube under N_2 for 20 min. The solvent was evaporated under reduced pressure, and the residue was purified by HPLC (LiChrosorb column, EtOAc/hexane (1:1)) to give **16** (35.0 mg, 0,111 mmol, 97%): colorless oil: ^1H NMR ($CDCl_3$) δ 7.48–7.30 (m, 6 H), 3.74 (s, 3 H), 3.72 (s, 3 H), 3.20–2.70 (m, 6 H); IR (film) 1730, 1596, 759 cm^{-1}; MS (EI) m/z 314 (M^+), 283, 195, 61 (100). Anal. Calcd for $C_{17}H_{18}N_2O_4$: C, 64.96; H, 5.77; N, 8.91. Found: C, 64.87; H, 5.76; N, 8.88.

Dimerization of 1-Phenyl-4,6-dihydrothieno[3,4-*c*]pyrazole (10). A solution of the sulfone **10** (50.0 mg, 0.213 mmol) in toluene (4.0 mL) was heated at 180 °C in a sealed tube under N_2 for 20 min. The solvent was evaporated under reduced pressure, and the residue was purified by HPLC (LiChrosorb column, EtOAc/hexane (2:1)) to give **17** (9.1 mg, 0,027 mmol, 12%), **18** (4.0 mg, 0.012 mmol, 6%), and the mixture of **19**–**22** which could not be separated by HPLC (total 2.0 mg, 0.006 mmol, 3%). Compound **17**: white solid; mp 171–172 °C; ^1H NMR ($CDCl_3$) δ 7.48–7.25 (m, 10 H), 7.43 (s, 2 H), 3.02 (s, 8 H); IR (KBr) 2929, 1598, 1387, 765 cm^{-1}; MS (EI) m/z 340 (M^+, 100), 325, 249, 183, 169; HRMS calcd for $C_{22}H_{20}N_4$ 340.1688, found 340.1690. The ^1H NMR spectrum of compound **17** showed its purity to be greater than 95%. Compound **18**: colorless oil; ^1H NMR ($CDCl_3$) δ 7.50–7.30 (m, 12 H), 3.20–3.08 (m, 4 H), 3.03–2.90 (m, 4 H); IR (film) 1596, 1497, 1386, 761 cm^{-1}; MS (EI) m/z 340 (M^+), 325, 249, 171 (100); HRMS calcd for $C_{22}H_{20}N_4$ 340.1688, found 340.1696. The ^1H NMR spectrum of compound **18** showed its purity to be greater than 95%. Compounds **19**–**22**: colorless oil; ^1H NMR ($CDCl_3$) δ 8.10–7.00 (m, 12 H), 5.16 (s, 1 H), 4.77 (s, 1 H), 3.10–1.80 (m, 6 H); δ 7.60–7.00 (m, 12 H), 5.10 (s, 1 H), 4.67 (s, 1 H), 3.10–1.80 (m, 6 H); δ 7.60–7.00 (m, 12 H), 4.72 (bs, 1 H), 3.97 (bs, 1 H), 3.10–1.80 (m, 6 H); δ 7.60–7.00 (m, 12 H), 3.75 (bs, 1 H), 3.66 (bs, 1 H), 3.10–1.80 (m, 6 H); IR (film) 2925, 1593, 1491, 755 cm^{-1}; MS (EI) m/z 340 (M^+, 100), 249, 169; HRMS calcd for $C_{22}H_{20}N_4$ 340.1688, found 340.1645.

Hexahydroindeno[4,5-*c*]pyrazole (24) and 5-(1,5-Hexadienyl)-4-methyl-1-phenylpyrazole (25). A solution of the sulfone **15** (16.0 mg, 0.0529 mmol) in toluene (2.0 mL) was heated at 180 °C in a sealed tube under N_2 for 30 min. The solvent was evaporated under reduced pressure, and the residue was purified by HPLC (LiChrosorb column, EtOAc/hexane (3:2)) to give **24** (8.1 mg, 0.034 mmol, 63%) and **25** (3.0 mg, 0.013 mmol, 24%). Compound **24**: colorless oil; ^1H NMR ($CDCl_3$) δ 7.53–7.27 (m, 6 H), 3.22 (td, J = 7.6, 7.6 Hz, 1 H), 2.85–0.90 (m, 1 H); IR (film) 2938, 1597, 1496, 1388, 978, 759 cm^{-1}; MS (EI) m/z 238 (M^+, 100), 209, 195, 170, 77; HRMS calcd for $C_{16}H_{18}N_2$ 238.1470, found 238.1476. The ^1H NMR spectrum of compound **24** showed its purity to be greater than 95%. Compound **25**: colorless oil; ^1H NMR ($CDCl_3$) δ 7.46–7.30 (m, 6 H), 6.21 (d, J = 16.2 Hz, 1 H), 5.99 (dt, J = 16.2, 6.2 Hz, 1 H), 5.92–5.71 (m, 1 H), 5.10–4.97 (m, 2 H), 2.35–2.15 (m, 4 H), 2.18 (s, 3 H); IR (film) 2925, 1597, 1497, 1383, 968, 910, 761, 694 cm^{-1}; MS (EI) m/z 238 (M^+), 197 (100), 186, 130, 77. HRMS calcd for $C_{16}H_{18}N_2$ 238.1470, found 238.1476. The ^1H NMR spectrum of compound **25** showed its purity to be greater than 95%.

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Supplementary Material Available: ^1H NMR spectra of most compounds (14 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.