Registry No. 1a, 54625-55-7; 1b, 615-36-1; 2a, 15050-24-5; 2b, 81245-91-2; 6, 31965-37-4; 7, 65027-11-4; 8, 19357-57-4; 9, 81245-92-3; 10, 79844-42-1; 11, 79854-96-9; 12, 79844-43-2; 13, 79844-44-3; 14, 79844-45-4; 15, 79844-46-5; 17, 79844-47-6; 18, 72952-48-8; 19, 81255-43-8; 20, 81245-93-4; 21, 81245-94-5; 22, 81245-95-6; 23, 3415-35-8; 24, 81245-96-7; 25, 81245-97-8; 26, 31965-37-4; 27, 34231-78-2; 28, 81245-98-9; 29, 81245-99-0; 30, 81246-00-6; 4-ClC_6H_4NHMe, 932-96-7; Cbz-Gly-OH, 1138-80-3; sarcosine, 107-97-1.

Isoxazolines by Cycloadditions of Mesitonitrile Oxide with Benzo[*b*]thiophene *S*-Oxide and *S*,*S*-Dioxide. Structural Studies, Theoretical Explanations, and Kinetics

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1,3-Dipolar cycloadditions of mesitonitrile oxide have been investigated with benzo[*b*]thiophene *S*-oxide and *S*,*S*-dioxide derivatives having a methyl, phenyl, piperidino, chloro, or bromo substituent on the active thiophene double bond. These dipolarophiles are more reactive than the original sulfur compound. The *S*-oxide and *S*,*S*-dioxide derivatives show nearly the same ability to form adducts. Among the two possible regioisomers, only one, the 2,3-dihydrobenzo[*b*]thieno[2,3-*d*]isoxazolines are formed. The regioselectivity is discussed in terms of frontier molecular orbital interactions on the basis of the photoelectronic spectra (IPs) and CNDO/S calculations. There is no stereoselectivity with the *S*-oxide compounds, and both syn and anti adducts are obtained. The chloro and bromo derivatives do not lead to any adduct.

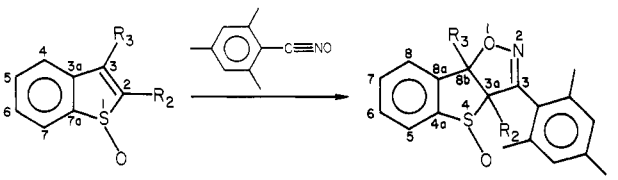
1,3-Dipolar cycloaddition reactions have been investigated for a long time, and their synthetic applications lead to various heterocycles.[1-8] Numerous studies based on quantum calculations have been carried out,[4-6] and the mechanism has been discussed at length.[7,8] Only a few reports are available on cycloaddition reactions involving a thiophene or benzo[*b*]thiophene ring.[9,10] Some adducts have been reported in the benzo[*b*]thiophene *S*,*S*-dioxide series without any stereochemical determinations.[11-13] The benzo[*b*]thiophene *S*-oxide series, whose synthesis has been extensively developed in our laboratory, remain to be investigated.[14,15]

Oxidation of the sulfur atom in benzo[*b*]thiophene compounds to a sulfoxide or a sulfone strongly decreases their aromatic character[16-18] and leads to a double bond mostly localized between C_2 and C_3. These oxidized compounds are more reactive with 1,3-dipoles such as mesitonitrile oxides than with benzo[*b*]thiophene itself.

Results and Discussion

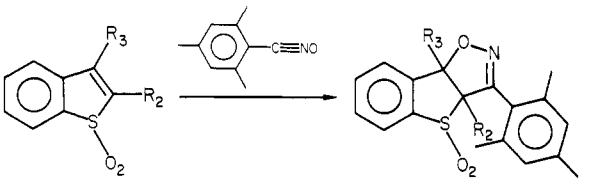
Cycloaddition of benzo[*b*]thiophenes and mesitonitrile oxide can lead to two different types of isomers, depending on the bonding of the oxygen atom of the dipole with C_2 or C_3 of the dipolarophile double bond. We call the two possible regioisomers, respectively, I (O–C_3) and II (O–C_2). Stereoisomers are formed only in the *S*-oxide series, according to the positions of the S–O bond and the substituent in C_{3a} being syn (on the same side of the benzo[*b*]thiophene plane) or anti (one on each side). In the case of a cycloaddition with the sulfone series, only two adducts

Scheme I. Experimental Results with Benzo[*b*]thiophene *S*-Oxide and *S*,*S*-Dioxide Series



1a, R_2 = H; R_3 = CH_3
c, R_2 = H; R_3 = C_6H_5

2a-syn, 2a-anti
2c-syn, 2c-anti



3, R_2 = H; R_3 = H
a, R_2 = H; R_3 = CH_3
b, R_2 = CH_3; R_3 = H
c, R_2 = H; R_3 = C_6H_5
d, R_2 = H; R_3 = 

4, R_2 = H; R_3 = H
a, R_2 = H; R_3 = CH_3
b, R_2 = CH_3; R_3 = H
c, R_2 = H; R_3 = C_6H_5
d, R_2 = H; R_3 = 

can be formed, regioisomers I and II, while addition to a sulfoxide can lead to four adducts: two epimers, syn and

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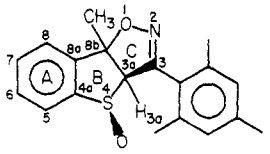
0022-3263/82/1947-2461$01.25/0

Table I. Proton NMR Data of the Adducts[a]

	chemical shift, δ			
			CH_3	
compd	R_3	R_2	ortho (s)	para (s)
2a-syn	1.95 (s, CH_3)	5.15 (s, H)	2.38	2.28
2a-anti	2.15 (s, CH_3)	4.78 (s, H)	2.15	2.31
2c-syn		5.23 (s, H)	2.19	2.25
2c-anti		4.97 (s, H)	2.10	2.28
4	6.46 (d, H, J = 9.5 Hz)	5.37 (d, J = 9.5 Hz)	2.24	2.32
4a	2.07 (s, CH_3)	4.93 (s, H)	2.20	2.30
4b	5.00 (s, H)	1.45 (s, CH_3)	2.06, 2.40	2.28
4c		5.14 (s, H)	2.29	2.39
4d		5.78 (s, H)	2.21	2.28
	1.56-1.70 (m, piperidino H)			

[a] s = singlet, d = doublet, and m = multiplet.

Table II. Characteristic X-ray Data for Adduct 2a-anti



Dihedral Angles, deg			
H-C_{3a}, C_{8b}-CH_3	12.9	O-S_4, C_{3a}-H	37.7
C_3-C_{3a},C_{8b}-O_1	18.1	O-S_4,$C_{3a}C_3$	161.5
Junction of Heterocycles, deg			
H-$C_{3a}C_{8b}$	117.2	C_{3a},C_{8b}-CH_3	115.6
Angles of the Planes, deg			
A, B	3.2	B, C	98

anti for each regioisomer I and II.

Our experimental results, reported in Scheme I, concern the cycloaddition of mesitonitrile oxide with the benzo[*b*]thiophene *S*-oxide and *S*,*S*-dioxide series containing various substituents on the active C_2=C_3 double bond and show no significant difference between the sulfoxide and the sulfone series in their ability to form adducts.

In the 2-substituted benzo[*b*]thiophene series, 1,3-cycloaddition is observed only with the 2-methyl *S*-dioxide derivative **3b**. In the 3-substituted series, cycloadducts are obtained by starting from the 3-methyl (**1a**, **3a**), 3-phenyl (**1c**, **3c**), and 3-piperidino (**3d**) derivatives and from the nonsubstituted sulfone compound **3**. The chloro or bromo derivatives do not lead to any adduct.

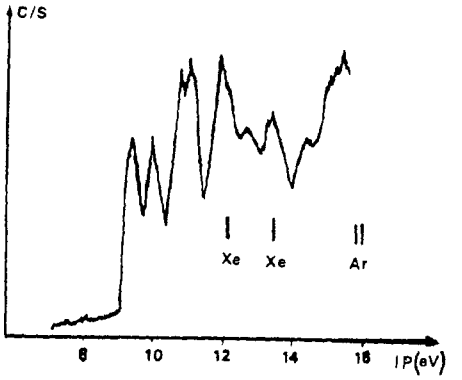


Figure 1. Photoelectronic spectrum of benzo[*b*]thiophene 1,1-dioxide (**3**).

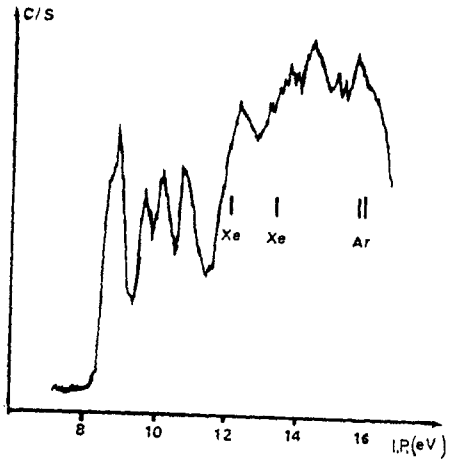


Figure 2. Photoelectronic spectrum of 3-methylbenzo[*b*]-thiophene 1-oxide (**1a**).

Sulfoxide Series. As shown in Scheme I, the reaction of excess mesitonitrile oxide with 3-methylbenzo[*b*]-thiophene 1-oxide (**1a**) in refluxing benzene led to the two diastereoisomer adducts, i.e., **2a**-syn and **2a**-anti in a 1:1 ratio. As reported in a previous paper,[15] the structure of the regioisomer has been determined by catalytic opening of the isoxazoline leading to the corresponding imine and confirmed by X-ray analysis of **2a**-anti.

The ^{1}H NMR assignments of the adduct **2a**-anti reported in Table I show that the chemical shift of H_{3a}, eclipsed with the S–O bond, is situated at higher field (δ 4.78). As expected, in the second diastereoisomer, **2a**-syn, the chemical shift of H_{3a} is at lower field (δ 5.15; Δδ = 0.37 ppm).

Reaction of mesitonitrile oxide and 3-phenylbenzo[*b*]-thiophene 1-oxide (**1c**) under the same conditions as above also led to two diastereoisomers, **2c**-syn and **2c**-anti, in a 1:3 ratio.

The syn–anti structure **2a** is confirmed by the crystallographic data in Table II.

Sulfone Series. Heating a mixture of mesitonitrile oxide and benzo[*b*]thiophene 1,1-dioxide (**3**) in refluxing benzene for 48 h resulted in the formation of only the single adduct **4** (yield 71%). In the same way, starting from the 3-methyl (**3a**), 3-phenyl (**3c**), and 3-piperidino (**3d**) derivatives, after reflux, in the appropriate solvent, we obtained respectively **4a**, **4c**, and **4d**.

The ^{1}H NMR spectrum of **4** (Table I) shows two doublet signals (J = 9.5 Hz) at δ 5.37 (1 H) and 6.46 (1 H). In comparison with the NMR data of adduct **4a**, the signal at higher field is assigned to H_{3a}, located at the α-position with respect to the sulfone group. In adduct **4** the coupling

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Table III. Vertical Ionization Potentials (eV) of Reactants

(a) Mesitonitrile Oxide

Π_1	n_O	Π_2	Π_3	Π_4
8.37	9.05	9.50	10.29	11.65

(b) Benzo[*b*]thiophene Sulfone Derivatives

compd	R_2	R_3	Π_1	Π_2	Π'_{SO}	Π_3	n_{Br}	$n_{O_1} + n_{O_2}$	n_{Cl}
3	H	H	9.32	9.88	10.60	10.95		11.82	
3a	H	Me	9.20	9.80	10.55	10.70		11.80	
3b	Me	H	9.10	9.80	10.45	10.85		11.70	
3e	Cl	H	9.25	10.00	10.80	11.00			11.95
3f	H	Cl	9.45	10.05	10.80	10.95			12.00
3g	Br	H	9.10	9.95	10.55	10.85	11.45	12.10	
3h	H	Br	9.40	10.00	10.70	10.70	11.52	12.10	

(c) Benzo[*b*]thiophene Sulfoxide Derivatives

compd	R_2	R_3	n_O-n_S	Π_1	Π_2	Π'_{SO}	n_{Br}	3	n_{Cl}
1a	H	Me	8.72	8.89	9.66	10.13		10.75	
1b	Me	H	8.75	8.75	9.64	10.13		10.84	
1d	Me	Me	8.40	8.62	9.50	9.98		10.46	
1e	Cl	H	9.10	9.10	9.90	10.50		10.95	11.85
1f	H	Cl	8.95	9.18	9.86	10.50		10.80	11.79
1g	Cl	Cl	9.00	9.28	10.00	10.80		10.80	12.05
1h	Br	H	9.10	9.10	9.90	10.40	10.78	11.20	
1i	H	Br	8.95	9.17	9.93	10.30	10.57	11.20	

constant (J_{3a-8b} = 9.5 Hz) of H_{3a} and H_{8b} located at the junction of the heterocycles is in agreement with a dihedral angle close to 10°, consistent with the X-ray study of adduct **2a**-anti and in accordance with the cis nature of the cycloaddition.

In the case of the 2-methyl dioxide derivative **3b**, despite the hindering of C_2 by the CH_3 group, it is possible to get the single adduct **4b** (yield 49%). From the NMR spectral data in Table I the *o*-methyl groups are not equivalent (δ 2.06 and 2.40) due to hindered rotation of the mesityl group.

In all these series, compounds with chloro, bromo on C_2 or C_3, dichloro, dimethyl, or dibromo substituents do not react.

Theoretical Explanations. We investigated the electronic structures of the dipoles and dipolarophiles in order to determine in the hypothesis of a concerted approach[19] the factors which are responsible for the regioselectivity. For this purpose we recorded the photoelectronic spectra of the compounds. The general shapes are given in Figures 1 and 2 for a typical sulfone and sulfoxide, and the ionization potentials (IPs) are listed in Table III for mesitonitrile oxide and for a series of sulfoxide and sulfone derivatives. The assignments have been done on the basis of CNDO/S calculations and are in complete agreement with the analysis of the effects of substituents. In Table III, the first IP associated with the HOMO (Π symmetry) of mesitonitrile oxide is clearly separated from the next IP. The CNDO/S calculations for this compound also show the energy of the LUMO to be much lower than the energy of the other unoccupied levels. We also note such an energetic gap in Table IIIb and Figure 1 for the sulfone series. On the other hand, the sulfoxide series show two occupied Π orbitals which are nearly degenerate (Table IIIc, Figure 2) and a significant localization on the reaction sites C_2 and C_3 (Figure 3b). In these sulfoxide compounds the HOMO-1, the first occupied orbital, corresponds to the antibonding combination n_s-n_o of the sulfur and oxygen doublets. The HOMO-1 presents the same symmetry as the HOMO-2 (Π system) on carbon atoms 2 and 3. The fourth occupied MO, called Π'_{SO}, is associated with the Π

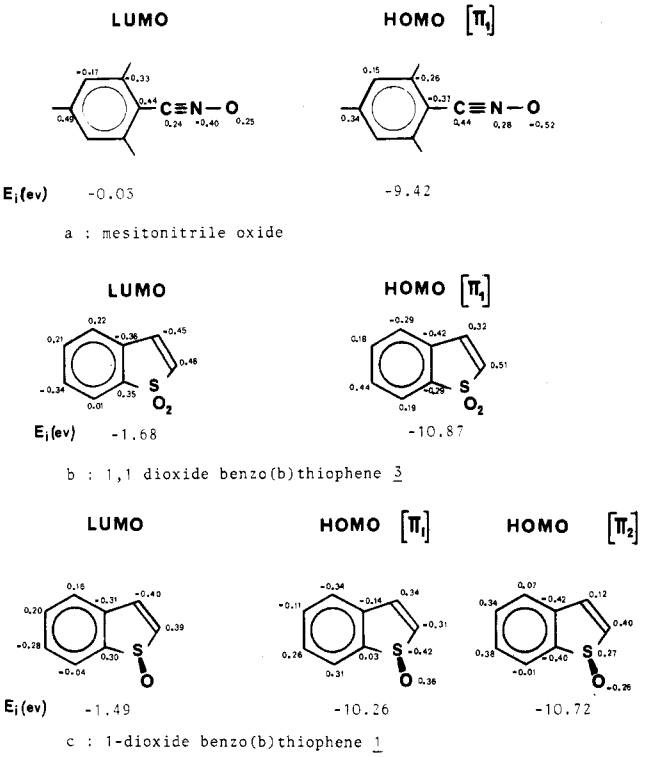

Figure 3. Calculated frontier molecular orbitals by CNDO/S method (eigenvectors and eigenvalues).

bond of the sulfoxide group and is orthogonal to the Π system of the benzothiophene ring.[20]

According to perturbation theory, the molecular orbital interactions which stabilize on approach are a function of the overlap of the concerned orbitals and also of the inverse of their energy separation. The HOMO dipole–LUMO dipolarophile interaction (Figure 3) is the strongest because of the energy separation, particularly in the case of sulfones. However, this interaction does not govern the regioselectivity since the coefficients of the LUMOs on

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Table IV. Rate Constants of Cycloaddition Reactions

dipolarophiles	k(disappearance), L mol^{-1} s^{-1}	k(appearance), L mol^{-1} s^{-1}	adducts
BTO_2 (3)	1×10^{-3} (±6%)	1×10^{-3} (±2%)	4
3-MeBTO_2 (3a)	9×10^{-5} (±6%)	10×10^{-5} (±5%)	4a
3-MeBTO (1a)	15×10^{-5} (±5%)	14×10^{-5}: $k_{anti} = 9 \times 10^{-5}$ (±6%)	2a-anti
		$k_{syn} = 5 \times 10^{-5}$ (±5%)	2a-syn

carbon atoms 2 and 3 are nearly the same, and this favors both approaches. Now, considering the HOMO dipolarophile–LUMO dipole interaction, one notes that the coefficients are nearly the same at the ends of the dipole, but this orbital shows a high localization with the same sign on the adjacent carbon atom (Figure 3a).

With the benzo[*b*]thiophene sulfone, the approach corresponding to the most efficient overlap will occur between C_2 (0.51) and $C_3 + C_4$ of the dipole, thus leading to the regioisomer I that has been obtained experimentally. In the case of the benzo[*b*]thiophene sulfoxide we take into account the HOMO-2 because HOMO-1, mainly located on the S–O group, has nearly the same coefficients on C_2 and C_3; as for the sulfone, we also conclude formation of regioisomer I. The 3-phenyl and 3-piperidino dipolarophiles show the same characteristics.

In conclusion we can say that the regioselectivity is governed by the HOMO dipolarophile–LUMO dipole interaction. The fact that there is no reaction with the 2-methylbenzo[*b*]thiophene sulfoxide (**1b**) can be correlated with the changes in the structure of the frontier orbitals, the localization being inverted in the LUMO and decreasing drastically in the HOMO. Nevertheless, on the basis of the frontier orbital interactions, there is no evidence for the absence of reaction observed with the 2- or 3-halogenated benzo[*b*]thiophene derivatives. The substitution introduces little change in the electronic structures and the energy levels of the HOMOs and LUMOs. We are now investigating a different theoretical approach to the problem.

Kinetic Studies. Dipolar cycloadditions are bimolecular reactions, and the kinetic constants have been determined by HPLC for the compounds **1a**, **3**, and **3a** (Table IV).

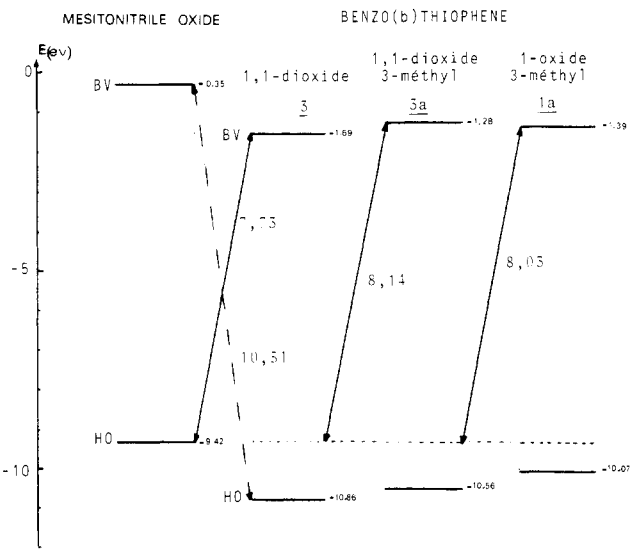
As shown, the sulfone is slightly less reactive than the sulfoxide, with formation of the anti stereoisomer being most rapid. Due to the linear structure of the dipole there are no secondary interactions as in the case of nitrone cycloadditions,[21,22] and the two paths of attack are very similar, with $\delta\Delta E_{act} = 1.8$ J/mol.

As in the cycloaddition reactions in the alkene series,[23] steric effects seem to be significant, leading to a much lower reactivity for the methyl derivative ($k_{MeBTO_2}/k_{BTO_2} = 0.08$).

This result is in accordance with the theoretical prediction that "electron poor" olefins are more reactive than the corresponding electron rich ones.[8]

Scheme II shows the influence of the methyl group on the orbital levels of the substrates and of the dipole with an higher level for the corresponding LUMO and nearby identical levels for the sulfoxide and the sulfone, in accordance with the identical kinetic reactivity.

Scheme II. Frontiers Orbital Energy of Mesitonitrile Oxide and Benzo[*b*]thiophene *S*-Oxide Derivatives



Experimental Section

General Methods. All melting points are uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker WP 80. The spectral data are given as δ values in parts per million from Me_4Si. Mass spectra were determined on a CEC-110C. Infrared spectra were obtained with a Perkin-Elmer 197.

Starting Materials. (a) Dipole. Mesitonitrile oxide was prepared according to the standard procedure.[24]

(b) Dipolarophiles. Sulfides. Benzo[*b*]thiophene is a commercial product and was purified by chromatography (SiO_2) or distillation. The benzo[*b*]thiophenes were synthesized according to standard procedures: 2-methyl,[25] 3-methyl,[26] 2,3-dimethyl,[27] 2-phenyl,[28] 3-phenyl,[29] 2-piperidino,[30] 3-piperidino,[30] 2-chloro,[31] 3-chloro,[32] 2,3-dichloro,[32] 2-bromo,[25] 3-bromo,[33] 2,3-dibromo.[29]

Sulfoxides. 3-Methyl- (**1a**), 2-methyl- (**1b**), 3-phenyl- (**1c**), 2,3-dimethyl- (**1d**), 2-chloro- (**1e**), 3-chloro- (**1f**), 2,3-dichloro- (**1g**), 2-bromo- (**1h**), and 3-bromobenzo[*b*]thiophene (**1i**) were prepared by oxidation (−13 °C) with metachloroperbenzoic acid of the corresponding sulfide. 2- and 3-piperidinobenzo[*b*]thiophene could not be oxidized.

Sulfones. Benzo[*b*]thiophene (**3**) and 3-methyl- (**3a**), 2-methyl- (**3b**), 3-phenyl- (**3c**), 2-chloro- (**3e**), 3-chloro- (**3f**), 2-bromo- (**3g**), and 3-bromobenzo[*b*]thiophene (**3h**) were obtained according to standard procedures.[32,34] 3-Piperidinobenzo[*b*]thiophene (**3d**) was prepared by Bordwell's procedure.[35]

Preparation of 4,4-Dioxo-3-(2,4,6-trimethylphenyl)-2,3-dihydrobenzo[*b*]thiopheno[2,3-*d*]isoxazoline (4). A solution of compound **3** (0.65 g, 2 mmol) and mesitonitrile oxide was

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refluxed in benzene (25 mL) for 12 h. After the solid materials (furoxane *N*-oxide) were removed by filtration, the solution was concentrated. Compound **4** was separated by chromatography on a silica column eluted with petroleum ether 95% and methylene chloride 5%: yield 70%; mp 253–254 °C; mass spectrum, *m/e* 327; IR 1150–1325 (SO_2) cm^{-1}. Anal. Calcd for $C_{18}H_{17}NO_3S$: C, 66.00; H, 5.21; N, 5.06. Found: C, 65.83; H, 5.35; N, 4.97.

Preparation of 4,4-Dioxo-3a-methyl-3-(2,4,6-trimethylphenyl)-2,3-dihydrobenzo[*b*]thiopheno[2,3-*d*]isoxazoline (4b). A solution of sulfone **3b** (2.05 g, 6 mmol) and mesitonitrile oxide (1.45 g, 9 mmol) was refluxed in benzene (50 mL) for 4 days. The furazan *N*-oxide was filtered off and the solution concentrated. Compound **4b** was obtained by crystallization of the residue in benzene: yield 47%; mp 181–182 °C; mass spectrum, *m/e* 341; IR 1160, 1315 (SO_2) cm^{-1}. Anal. Calcd for $C_{19}H_{19}NO_3S$: C, 66.86; H, 5.57; N, 4.11. Found: C, 66.63; H, 5.65; N, 4.10.

Preparation of 4,4-Dioxo-8b-methyl-3-(2,4,6-trimethylphenyl)-2,3-dihydrobenzo[*b*]thiopheno[2,3-*d*]isoxazoline (4a). A solution of sulfone **3a** (3.4 g, 10 mmol) and mesitonitrile oxide (2.4 g, 15 mmol) was refluxed in benzene during 8 h. The solution was filtered and concentrated, and the residue was crystallized in benzene. Compound **4a** was obtained: 74% yield; mp 223 °C; mass spectrum, *m/e* 341; IR 1160–1180, 1325 (SO_2) cm^{-1}. Anal. Calcd for $C_{19}H_{19}NO_3S$: C, 66.86; H, 5.57; N, 4.10. Found: C, 66.68; H, 5.89; N, 4.05.

Preparation of 4,4-Dioxo-8b-phenyl-3-(2,4,6-trimethylphenyl)-2,3-dihydrobenzo[*b*]thiopheno[2,3-*d*]isoxazoline (4c). A solution of **3c** (1.61 g, 4 mmol) and mesitonitrile oxide (0.96 g, 6 mmol) was refluxed in chloroform (25 mL) during 2 days. The solution was filtered and concentrated, and the residue was chromatographed on a silica column eluted with petroleum ether (96%)–methylene chloride (4%). Compound **4c** was obtained: 60% yield; mp 217–218 °C; mass spectrum, *m/e* 403; IR 1150, 1350 (SO_2) cm^{-1}. Anal. Calcd for $C_{24}H_{21}NO_3S$: C, 71.45; H, 5.25; N, 3.47. Found: C, 71.21; H, 5.27; N, 3.51.

Preparation of 4,4-Dioxo-8b-piperidino-3-(2,4,6-trimethylphenyl)-2,3-dihydrobenzo[*b*]thiopheno[2,3-*d*]isoxazoline (4d). A solution of **3d** (2.05 g, 5 mmol) and mesitonitrile oxide (1.2 g, 25 mmol) was refluxed in chloroform (50 mL) during 5 days. The solution was filtered and concentrated, and the residue was chromatographed on a silica column eluted with petroleum ether (90%)–methylene chloride (10%). Compound **4d** was obtained: 24% yield; mp 174 °C; mass spectrum, *m/e* 410; IR 1160, 1305 (SO_2) cm^{-1}. Anal. Calcd for $C_{23}H_{26}N_2O_3S$: C, 67.30; H, 6.39; N, 6.83. Found: C, 67.39; H, 6.45; N, 6.88.

Additions to Sulfoxides. Preparation of 4-Oxo-8b-methyl-3-(2,4,6-trimethylphenyl)-2,3-dihydrobenzo[*b*]thiopheno[2,3-*d*]isoxazoline (2a). A solution of compound **1a** (0.33 g, 1 mmol) and mesitonitrile oxide (0.24 g, 1.5 mmol) was refluxed in benzene (25 mL) for 2 days. The solution was filtered and concentrated, and the residue was chromatographed by silica TLC with chloroform (95%)–acetone (5%) as the eluent. Two compounds were obtained: **2a**-syn (30% yield), **2a**-anti (33% yield).

2a-syn: mp 213 °C; mass spectrum, *m/e* 325; IR 1040, 1060 (SO) cm^{-1}. Anal. Calcd for $C_{19}H_{19}NO_2S$: C, 70.15; H, 5.85; N, 4.31. Found: C, 69.18; H, 6.08; N, 4.35.

2a-anti: mp 178 °C; mass spectrum, *m/e* 325; IR 1035, 1055 (SO) cm^{-1}. Anal. Calcd for $C_{19}H_{19}NO_2S$: C, 70.15; H, 5.85; N, 4.31. Found: C, 69.79; H, 6.09; N, 4.22.

Preparation of 4-Oxo-8b-phenyl-3-(2,4,6-trimethylphenyl)-2,3-dihydrobenzo[*b*]thiopheno[2,3-*d*]isoxazoline (2c). A solution of compound **1c** (0.18 g, 0.4 mmol) and mesitonitrile oxide (0.116 g, 0.72 mmol) was refluxed in chloroform (20 mL) during 3 days. The solution was filtered and concentrated, and the residue was chromatographed on a silica column with petroleum ether (87%)–methylene chloride (13%). Two compounds were obtained **2c**-anti (24% yield) and **2c**-syn (8% yield).

2c-syn: mp 221–222 °C; mass spectrum, *m/e* 387; IR 1004, 1090 (SO_2) cm^{-1}. Anal. Calcd for $C_{24}N_{21}NO_2S$: C, 74.40; H, 5.46; N, 3.62. Found: C, 74.34; H, 5.40; N, 3.56.

2c-anti: mp 202–203 °C; mass spectrum, *m/e* 387; IR 1010, 1090 (SO_2) cm^{-1}. Anal. Calcd for $C_{24}H_{21}NO_2S$: C, 74.40; H, 5.46; N, 3.02. Found: C, 74.45; H, 5.48; N, 3.67.

Kinetic Studies. In refluxing chloroform, solutions of dipole, dipolarophile, and an internal standard, i.e., phenol, were prepared: (a) 1,1-dioxobenzo[*b*]thiophene (**3**, 0.0164 mol/L), dipole (0.207 mol/L), phenol (0.0154 mol/L); (b) 1,1-dioxo-3-methylbenzo[*b*]thiophene (**3a**, 0.0206 mol/L), dipole (0.218 mol/L), phenol (0.0198 mol/L); (c) 1-dioxo-3-methylbenzo[*b*]thiophene (**1a**, 0.0226 mol/L), dipole (0.222 mol/L), phenol (0.0190 mol/L).

The reaction kinetics were obtained by analyzing aliquots by HPLC with a UV detector at 265 nm. The pseudo-first-order kinetic constants were determined by least-squares analysis, and the given values are the result of at least three runs with a precision of about 6%. The column type and the eluent used were as follows: for **3**, silica (Hibar Merck), cyclohexane (65%)–methylene chloride (35%); for **3a**, silica (Hibar Merck), cyclohexane (70%)–methylene chloride (30%); for **1a**, μ-Bondapack (CN Waters), cyclohexane (85%)–chloroform (15%).

X-ray Analysis and Structure Determination of 2a-anti. The following data were obtained: $C_{19}H_{19}NO_2S$, orthorhombic, a = 8.597 (2) Å, b = 12.891 (2) Å, c = 15.464 (4) Å, space group $Pca2_1$, Z = 4.

The crystal was mounted on a Syntex $P2_1$ diffractometer, and Cu Kα radiation (λ = 1.541 79 Å) was used to a maximum 2θ value of 114°. A total of 1208 reflections were measured, and only 1165 of them had $I > 2.5\sigma(I)$. The intensities were corrected for Lorentz and polarization factors but not for absorption.

The structure was solved with the MULTAN 78 program.[36] The structure was then refined with the SHELX 76 program.[37] After three cycles of isotropic full-matrix least-squares refinement, R fell to 0.12, and after one cycle of anisotropic refinement R was 0.08. The H atom positions were assumed, and their corresponding parameters were inserted but not allowed to vary in the last cycle of anisotropic refinement (final R = 0.064).

Registry No. **1a**, 51500-43-7; **1b**, 33945-86-7; **1c**, 70445-87-3; **1d**, 70445-88-4; **1e**, 57147-28-1; **1f**, 63724-95-8; **1g**, 30834-33-4; **1h**, 57147-27-0; **1i**, 57147-26-9; *syn*-**2a**, 74410-57-4; *anti*-**2a**, 74372-98-8; *syn*-**2c**, 81445-43-4; *anti*-**2c**, 81390-94-5; **3**, 825-44-5; **3a**, 6406-91-3; **3b**, 6224-55-1; **3c**, 27183-55-7; **3d**, 1022-19-1; **3e**, 10133-41-2; **3f**, 21211-29-0; **3g**, 5350-05-0; **3h**, 16957-97-4; **4**, 81390-95-6; **4a**, 74372-99-9; **4b**, 81390-96-7; **4c**, 81390-97-8; **4d**, 81390-98-9; 2-methylbenzo[*b*]thiophene, 1195-14-8; 3-methylbenzo[*b*]thiophene, 1455-18-1; 2,3-dimethylbenzo[*b*]thiophene, 4923-91-5; 2-phenylbenzo[*b*]thiophene, 1207-95-0; 3-phenylbenzo[*b*]thiophene, 14315-12-9; 2-piperidinobenzo[*b*]thiophene, 40584-57-4; 3-piperidinobenzo[*b*]thiophene, 33880-37-4; 2-chlorobenzo[*b*]thiophene, 7342-85-0; 3-chlorobenzo[*b*]thiophene, 7342-86-1; 2,3-dichlorobenzo[*b*]thiophene, 5323-97-7; 2-bromobenzo[*b*]thiophene, 5394-13-8; 3-bromobenzo[*b*]thiophene, 7342-82-7; 2,3-dibromobenzo[*b*]thiophene, 6287-82-7; mesitonitrile oxide, 2904-57-6.

Supplementary Material Available: Tables of atomic coordinates and thermal parameters and two figures showing stereoscopic and perspective views of the structure of **2a**-anti (5 pages). Ordering information is given on any current masthead page.

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