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Reactions of electron-withdrawing thiophene 1,1-dioxides with furans. A novel reaction pathway

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Reactions of thiophene dioxides containing electron-withdrawing substituents with furans were studied. The reactions with unsubstituted furan followed the inverse-electron-demand Diels—Alder mechanism. Subsequent elimination of sulfur dioxide from the adduct afforded products of the tetrahydrobenzofuran series. The reactions with substituted furans gave benzylcarbonyl compounds in high yields. The observed regiochemistry of the reaction was explained in terms of the frontier orbital theory using the calculated orbital coefficients.

Key words: thiophene 1,1-dioxides with electron-withdrawing substituents, the Diels—Alder reaction, substituted furans, benzylcarbonyl compounds.

The Diels—Alder reaction with furans as a 4π-component is a well-studied transformation.[1] The theoretical value and applications of furans in cycloaddition reactions is difficult to overestimate. The use of furans in various cycloaddition reactions remains so far in demand in all areas of synthetic organic chemistry. Furan derivatives show an important ability to react with various dienophiles, giving [4+2] cycloadducts with a six-membered fragment capable of further transformations. Because of this, they are successfully employed in the synthesis of natural compounds[2] and macromolecules[3] and used as protective groups.[4]

Reactions of furans with thiophene 1,1-dioxides are of particular attention. In these reactions, halogen- and alkyl-containing thiophene 1,1-dioxides serve as dienes, while furan acts as a dienophile. Intermediate cycloadducts with the bridging SO_2 group undergo spontaneous elimination of sulfur dioxide and a tandem rearrangement into benzylcarbonyl compounds.[5] Elimination of SO_2 followed by aromatization is a powerful driving force of this reaction that explains well the atypical behavior of furans as dienophiles. It is known[6] that thiophene dioxides containing no strong electron-withdrawing groups behave like electron-withdrawing dienes, reacting with dienophiles with elimination of SO_2 to give the cyclohexadiene system.

Earlier,[7] we have developed a convenient route to thiophene dioxides containing electron-withdrawing substituents. We have also studied the behavior of some of the compounds obtained in reactions with 1,3-dienes and found that these compounds are reactive dienophiles, in contrast to thiophene dioxides containing no strong electron-withdrawing substituents. For instance, they act as dienophiles in [4+2] cycloaddition reactions with open and cyclic 1,3-dienes to give both mono- and bisadducts.[8]

Because cycloaddition to various dienophiles is characteristic of furan and its derivatives, the possibility of carrying out reactions with new electron-withdrawing thiophene dioxides we synthesized is of great interest. In addition, reactions of thiophene dioxides with various furans have not been adequately investigated: only a few substituted thiophene dioxides have been studied and only two examples of reactions with unsubstituted furan have been reported.[5a,9]

Results and Discussion

Taking into account that electron-withdrawing thiophene dioxides can act as dienophiles, we expected the formation of 7-oxabicyclo[2.2.1]hept-5-ene (7-oxabornene) derivatives, which are usual adducts of furan with dienophiles.[1]

However, the major product (71%) of the reaction of thiophene dioxide **1a** with furan (Scheme 1) was 4,7-dichloro-3a,7a-dihydro-1-benzofuran (**2**). Thus, we isolated for the first time an intermediate with the stable furan ring, which opened up new potentialities of this reaction.

We assumed that this is also valid for other electron-withdrawing substituents in the thiophene ring.

Indeed, thiophene dioxides **1b—d** containing strong electron-withdrawing SO_2Me and CN groups easily reacted with furan in CH_2Cl_2 at room temperature in 1 h. The thiophene dioxides acted as dienes, which was evident from the evolution of SO_2 in all cases; however, the

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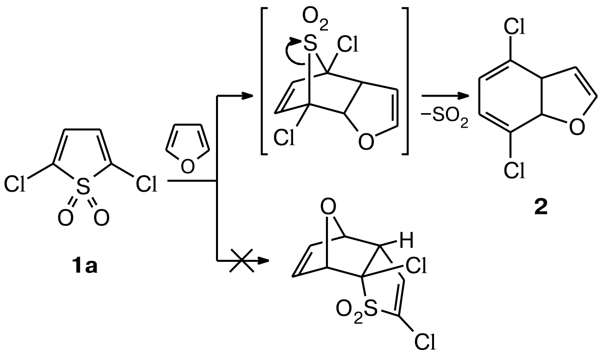
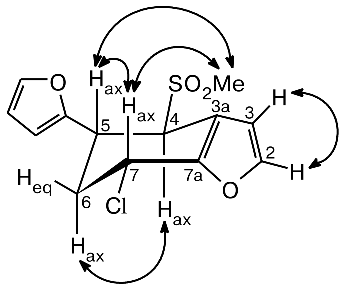
Scheme 1



products obtained were structurally different from compound **2**.

According to 2D NMR data (NOESY, COSY, HMBC, and HSQC), the compounds obtained contain two furan fragments and have a structure of 5-(2-furyl)tetrahydrobenzofurans. The NOESY correlations for compound **3a** are shown below as an example.

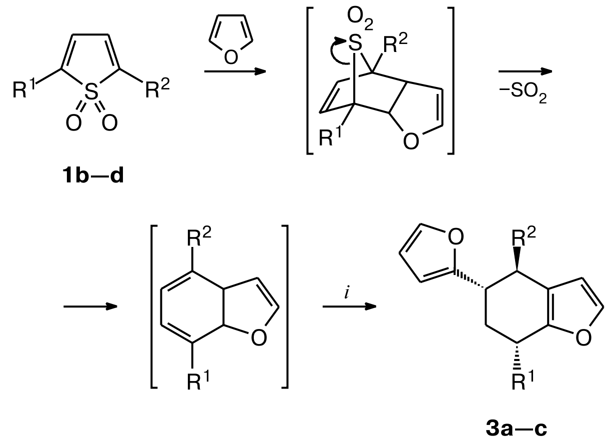


The formation of the furan ring fused with the six-membered ring was also detected by ^{1}H NMR spectroscopy: The signals for two protons in this furan ring are separate from other signals and appear as two characteristic doublets (J = 6.5 Hz). To specify the exact configurations of the compounds obtained, we correlated the coupling constants corresponding to all the protons in the cyclohexane ring with the characteristic constants for substituted cyclohexanes.[10] The H(7) and H(4) protons were unambiguously located in axial positions because they showed only two vicinal couplings with characteristic constants of 10.4 and 11.1 Hz, respectively. Thus, the reaction yields the thermodynamically most stable isomer in which all substituents are equatorial.

The reaction is of the general character: other electron-withdrawing thiophene 1,1-dioxides also gave tricyclic products **3b,c** in high yields (Scheme 2).

With unsymmetrical thiophene 1,1-dioxides containing two different substituents, two regioisomeric adducts can be obtained. However, only one of the possible regioisomers was isolated for each thiophene dioxide **1b**—**d**.

Scheme 2



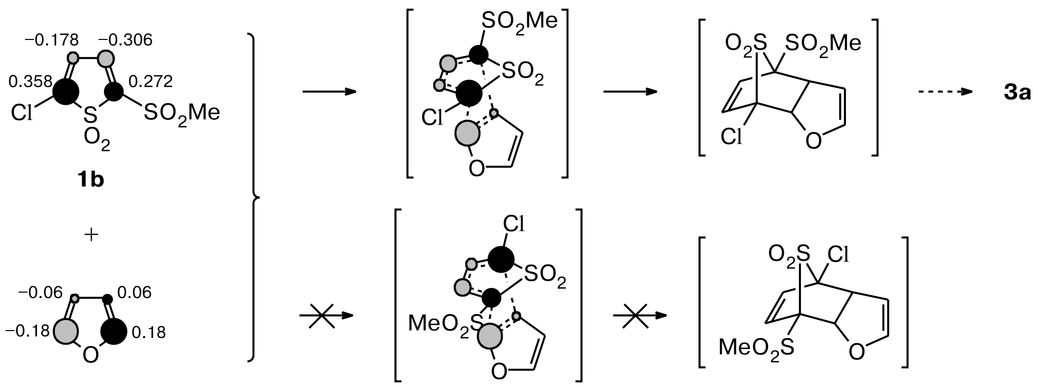
i. 1. Furan; 2. Isomerization.

Thiophene dioxide	R^1	R^2	Product	Yield (%)
1b	Cl	SO_2Me	**3a**	41
1c	Br	SO_2Me	**3b**	33
1d	Me	CN	**3c**	72

The first step of this transformation is the inverse-electron-demand Diels—Alder reaction. Cycloaddition reactions of this type are known to be controlled by the highest occupied molecular orbitals (HOMO) of a dienophile and the lowest unoccupied molecular orbitals (LUMO) of a diene.[11,12] To interpret the observed regioselectivity, we used quantum-chemical data for the LUMO of thiophene 1,1-dioxides[8c,13] and for the HOMO of furan.[11,12] In terms of the frontier molecular orbital theory,[1c,11] regioselectivity is due to overlap of the molecular orbitals with the highest coefficients of both the diene and dienophile in the transition state of the Diels—Alder reaction of thiophene dioxide with furan. The resulting strict orientation of the diene and the dienophile in the transition state makes the reaction extremely regioselective and predetermines the respective arrangement of the substituents in reaction products. A reaction of thiophene 1,1-dioxide **1b** with furan is shown in Scheme 3 as an example (the orbital coefficients are indicated). The regiochemistry of adducts obtained from other substituted thiophene dioxides is much the same.[8c]

The formation of products **3a**—**c** is probably due to a reaction of dihydrobenzofurans (Diels—Alder adducts) with an excess of furan. Reactions of thiophene dioxides containing strong electron-withdrawing groups (SO_2Me, CO_2Me, and CN) gave functionalized dihydrobenzofurans. The double bond in these products is activated for nucleophilic addition: its interaction with an excess of furan (Michael addition) followed by migration of the double bond yields compounds **3a**—**c**. Such a type of the Michael addition of furans is well known;[14] the driving

Scheme 3



force of the migration is the formation of an aromatic structure. Similar migrations catalyzed by rhodium(III) chloride have been described earlier[15] for furan systems.

Variation in the amount of furan (1, 1.5, and 0.5 equiv.) did not change the pathway of this reaction: we isolated only products **3a—c** and the unreacted thiophene dioxides **1b—d**.

To investigate the general character and regioselectivity of this process with respect to the furan component, we used 2-methylfuran (sylvan), 2,5-dimethylfuran, and methyl furan-2-carboxylate in the reaction.

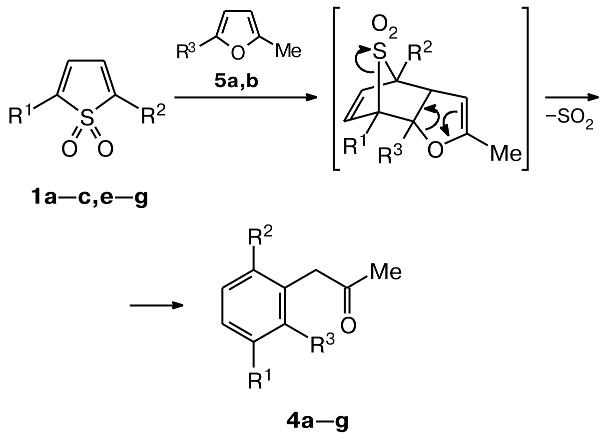
We found that these reagents exclusively yield benzylcarbonyl compounds, in contrast to the reactions with unsubstituted furan. Apparently, intermediate products in these cases, more rapidly undergo opening into the corresponding carbonyl compounds (for 2,5-dimethylfuran, the Michael addition is impossible).

Using a number of thiophene dioxides with electron-withdrawing substituents **1a—f** and substituted furans, we obtained previously unknown benzylcarbonyl compounds **4a—g** (Scheme 4).

The reaction opens up wide possibilities for the synthesis of functionalized benzylcarbonyl compounds; variation of thiophene dioxides and furans allows one to obtain carbonyl compounds with various substituents.

It should be noted that the regioselectivity of the addition of sylvan and methyl furan-2-carboxylate to all thiophene dioxides was 100%. We detected no adducts due to addition at the double bond with the methyl group. In this case, the observed regioselectivity can be explained by favorable electronic and steric effects. Thus, for thiophene dioxide **1b** and 2-methylfuran (**5a**), addition involved the side without the methyl group (Scheme 5).

Scheme 4



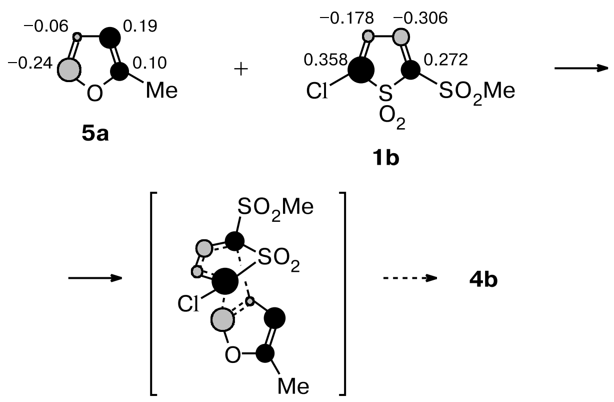
Thiophene dioxide	R1	R2
1e	Br	CO_2Me
1f	Me	SO_2Me
1g	SO_2Me	SO_2Me

Compound	R1	R2	R3	Yield (%)
4a	Cl	Cl	H	91
4b	Cl	SO_2Me	H	81
4c	Br	SO_2Me	H	70
4d	Br	CO_2Me	H	88
4e	Me	SO_2Me	H	95
4f	SO_2Me	SO_2Me	H	96
4g	SO_2Me	SO_2Me	Me	93

R^3 = H (**5a**), Me (**5b**)

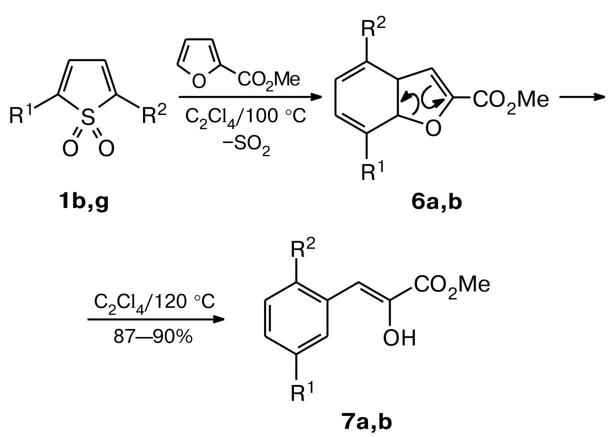
An interesting result was obtained from methyl pyromucate as a furan component and thiophene dioxides **1b,g**. Prolonged stirring of the reagents at room temperature in CH_2Cl_2 gave no products (monitoring by TLC), while heating under reflux very slowly yielded a mixture of two compounds. However, rapid heating of the reaction mixture in tetrachloroethylene to 100 °C resulted in the complete conversion of the starting thiophene dioxides and the quantitative formation of products **6a,b** (Scheme 6). Further heating of the reaction mixture in boiling tetrachloroethylene for 1 h gave the target benzylcarbonyl compounds **7a,b** in 87 and 90% yields, respectively. Apparently, isolation of substituted dihydrobenzo-

Scheme 5



furans **6a,b** became possible because of the presence of the electron-withdrawing ester group. Consequently, higher temperatures were required for rearrangement into benzylcarbonyl compounds.

Scheme 6



R^1 = Cl, R^2 = SO_2Me (**6a**, **7a**); R^1 = R^2 = SO_2Me (**6b**, **7b**)

Products **7a,b** exist in the enol form, which was confirmed by NMR and IR spectroscopy. For instance, the IR spectra of the benzylcarbonyl compounds obtained contain characteristic bands of the OH group at 3300 cm^{-1}.

Dihydrobenzofuran derivatives **6a,b** are by themselves interesting objects of investigation. Their oxidative aromatization can afford substituted derivatives of benzofurancarboxylic acids.

Thus, we studied the reactions of electron-withdrawing thiophene 1,1-dioxides with furans and isolated for the first time previously postulated reaction intermediates. In the case of thiophene dioxides containing strong electron-withdrawing groups, 5-(2-furyl)tetrahydrobenzofurans were obtained. The reactions of substituted furans with thiophene dioxides exclusively gave functionalized benzylcarbonyl compounds. The 100% regioselectivity of the cycloaddition of thiophene dioxides to furans is due to both orbital and steric factors.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer (400 and 100 MHz, respectively) in $CDCl_3$, CD_3CN, and DMSO-d_6 with Me_4Si as the internal standard. TLC was carried out on Merck $60F_{254}$ plates; column chromatography was carried out on silica gel (63—200 mesh, Merck).

Commercial reagents were used. Thiophene 1,1-dioxides were prepared as described earlier.[7]

4,7-Dichloro-3a,7a-dihydro-1-benzofuran (2). Freshly distilled furan (1 mL, 15.7 mmol) was added at 0 °C to a vigorously stirred solution of thiophene dioxide **1a** (1 mmol, 185 mg) in dry dichloromethane (10 mL). The reaction mixture was warmed to room temperature and stirred for 12 h. The solvent and the excess of furan were removed *in vacuo*. The residue was chromatographed on silica gel with hexane—ethyl acetate (1 : 1) as an eluent. The yield was 71%, colorless crystals, m.p. 135—136 °C. Found (%): C, 50.81; H, 3.14. $C_8H_6Cl_2O$. Calculated (%): C, 50.83; H, 3.20. ^1H NMR ($CDCl_3$), δ: 3.78—3.80 (m, 1 H, C(3a)H); 5.25 (s, 1 H, C(7a)H); 5.29—5.31 (m, 1 H, $C\underline{H}$=CH—O); 6.33 (d, 1 H, CH=$C\underline{H}$—O, J = 3.1 Hz); 6.41—6.43, 6.69—6.71 (both dd, 1 H each, C(5)$\underline{H}$—$C\underline{H}$, C(6)$\underline{H}$—$C\underline{H}$, J = 1.8 Hz, J = 5.9 Hz). ^{13}C NMR ($CDCl_3$), δ: 57.9, 80.9, 88.2, 130.2, 134.5, 135.1, 135.3.

Reactions of thiophene dioxides 1b—d with an excess of furan (general procedure). Freshly distilled furan (1 mL, 15.7 mmol) was added at 0 °C to a vigorously stirred solution or suspension of thiophene dioxide **1b—d** (1 mmol) in dry dichloromethane (10 mL). The reaction mixture was warmed to 15 °C, stirred at this temperature for 1—2 h, and then left at ~20 °C for ~14 h for the reaction to be completed. The solvent and the excess of furan were removed *in vacuo*. The residue was chromatographed on silica gel with hexane—ethyl acetate (1 : 1) as an eluent.

7-Chloro-5-(2-furyl)-4-methylsulfonyl-4,5,6,7-tetrahydro-1-benzofuran (3a). The yield was 41%, a light yellow oil. Found (%): C, 51.61; H, 4.33. $C_{13}H_{13}ClO_4S$. Calculated (%): C, 51.92; H, 4.36. ^1H NMR (CD_3CN), δ: 2.31—2.39, 2.70—2.77 (both m, 1 H each, C(6)CH_2); 2.99 (s, 3 H, SO_2Me); 3.61—3.68, 4.94—4.98 (both m, 1 H each, C(5)H, C(7)H); 5.10 (d, 1 H, $C\underline{H}SO_2C(4)H_3$, J = 10.4 Hz); 6.36 (d, 1 H, C(3)H, J = 6.5 Hz); 6.40 (m, 2 H, 4,3-furyl); 6.78 (d, 1 H, C(2)H, J = 6.5 Hz); 7.49 (br.s, 1 H, 5-furyl). ^{13}C NMR (CD_3CN), δ: 39.7, 40.5, 43.2, 71.9, 79.6, 109.7, 111.8, 121.0, 130.2, 141.0, 141.9, 144.4.

7-Bromo-5-(2-furyl)-4-methylsulfonyl-4,5,6,7-tetrahydro-1-benzofuran (3b). The yield was 33%, a yellow oil. Found (%): C, 45.11; H, 3.69. $C_{13}H_{13}BrO_4S$. Calculated (%): C, 45.23; H, 3.80. ^1H NMR ($CDCl_3$), δ: 1.92—1.99, 2.63—2.68 (both m, 1 H each, C(6)H_2); 2.95 (s, 3 H, SO_2Me); 3.48—3.59, 3.72—3.80 (both m, 1 H each, C(5)H, C(7)H); 5.07 (d, 1 H, $C\underline{H}SO_2C(4)H_3$, J = 11.6 Hz); 5.11 (d, 1 H, CH, J = 4.6 Hz); 6.30 (br.s, 1 H, 5-furyl); 6.45, 6.67 (both d, 1 H each, C(2)H, C(3)H, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 36.6, 41.3, 42.3, 63.2, 78.5, 99.2, 123.6, 129.1, 132.0, 133.8, 139.9, 142.8.

5-(2-Furyl)-7-methyl-4,5,6,7-tetrahydro-1-benzofuran-4-carbonitrile (3c). The yield was 72%, a yellow oil. Found (%): C, 73.95; H, 5.43. $C_{14}H_{13}NO_2$. Calculated (%): C, 73.99; H, 5.77. ^{1}H NMR ($CDCl_3$), δ: 1.61 (br.s, 1 H); 2.12 (s, 3 H, Me); 2.24 (d, 1 H, J = 1.8 Hz); 3.47 (br.d, 1 H, J = 1.8 Hz); 4.99, 5.59 (both br.s, 1 H each); 6.26, 6.40 (both br.s, 1 H each, 4,3-furyl); 6.53—6.55, 6.69—6.71 (both m, 1 H each); 6.76—6.78 (dd, 1 H, J = 1.8 Hz, J = 5.3 Hz). ^{13}C NMR (CD_3CN), δ: 39.7, 40.5, 43.2, 71.9, 79.6, 109.7, 111.8, 121.0, 130.2, 141.0, 141.9, 144.4.

Synthesis of benzylcarbonyl compounds (general procedure). An appropriate furan (5 mmol) (2,5-dimethylfuran in the synthesis of **3g** and 2-methylfuran in the other cases) was added at 0 °C to a solution of thiophene dioxide (1 mmol) in dichloromethane (5 mL). The reaction mixture was kept at this temperature for 1 h and concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2, passed through a layer of silica gel (1—2 g), and concentrated.

1-(2,5-Dichlorophenyl)acetone (4a). The yield was 91%, a colorless oil. Found (%): C, 53.11; H, 3.80. $C_9H_8Cl_2O$. Calculated (%): C, 53.23; H, 3.97. ^{1}H NMR ($CDCl_3$), δ: 2.23 (s, 3 H, CH_3CO); 3.81 (s, 2 H, CH_2); 7.19—7.21 (m, 2 H); 7.30—7.32 (m, 1 H). ^{13}C NMR ($CDCl_3$), δ: 29.2, 48.3, 128.9, 129.0, 130.1, 131.4, 132.0, 133.7, 201.6.

1-(5-Chloro-2-methylsulfonylphenyl)acetone (4b). The yield was 81%, colorless crystals, m.p. 140—141 °C. Found (%): C, 48.51; H, 4.82. $C_{10}H_{11}ClO_3S$. Calculated (%): C, 48.68; H, 4.49. ^{1}H NMR ($CDCl_3$), δ: 2.31 (s, 3 H, CH_3CO); 3.01 (s, 3 H, SO_2CH_3); 4.25 (s, 2 H, CH_2); 7.20 (d, 1 H, J = 2.1 Hz); 7.45 (dd, 1 H, J = 2.1 Hz, J = 8.6 Hz); 7.94 (d, 1 H, J = 8.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 30.1, 44.4, 48.1, 128.6, 131.6, 133.4, 136.3, 137.5, 140.0, 204.9.

1-(5-Bromo-2-methylsulfonylphenyl)acetone (4c). The yield was 70%, a colorless oil. Found (%): C, 41.34; H, 3.80. $C_{10}H_{11}BrO_3S$. Calculated (%): C, 41.25; H, 3.81. ^{1}H NMR ($CDCl_3$), δ: 2.31 (s, 3 H, CH_3CO); 3.03 (s, 3 H, SO_2CH_3); 4.22 (s, 2 H, CH_2); 7.19 (d, 1 H, J = 2.0 Hz); 7.41 (dd, 1 H, J = 2.0 Hz, J = 8.5 Hz); 7.90 (d, 1 H, J = 8.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 29.8, 44.0, 47.9, 128.3, 131.1, 133.2, 135.8, 137.1, 139.4, 206.1.

Methyl 4-bromo-2-(2-oxopropyl)benzoate (4d). The yield was 88%, a yellow oil. Found (%): C, 41.34; H, 3.80. $C_{11}H_{11}BrO_3$. Calculated (%): C, 41.25; H, 3.81. ^{1}H NMR ($CDCl_3$), δ: 2.31 (s, 3 H, CH_3CO); 3.86 (s, 3 H, CO_2CH_3); 4.09 (s, 2 H, CH_2); 7.37 (d, 1 H, J = 2.0 Hz); 7.51 (dd, 1 H, J = 2.0 Hz, J = 8.3 Hz); 7.92 (d, 1 H, J = 8.3 Hz). ^{13}C NMR ($CDCl_3$), δ: 29.6, 48.5, 52.1, 122.7, 123.3, 127.5, 130.2, 131.0, 134.6, 169.4, 205.8.

1-(5-Methyl-2-methylsulfonylphenyl)acetone (4e). The yield was 95%, a colorless oil. Found (%): C, 58.41; H, 6.12. $C_{11}H_{14}O_3S$. Calculated (%): C, 58.38; H, 6.24. ^{1}H NMR ($CDCl_3$), δ: 2.29 (s, 3 H, CH_3CO); 2.38 (s, 3 H, CH_3); 2.99 (s, 3 H, SO_2CH_3); 4.23 (s, 2 H, CH_2); 7.00 (s, 1 H); 7.26, 7.87 (both d, 1 H each, J = 8.1 Hz). ^{13}C NMR ($CDCl_3$), δ: 20.9, 29.6, 44.0, 47.9, 128.6, 129.7, 133.7, 135.6, 144.3, 205.4.

2,5-[Bis(methylsulfonyl)phenyl]acetone (4f). The yield was 96%, colorless crystals, m.p. 201 °C. Found (%): C, 45.51; H, 4.82. $C_{11}H_{14}O_5S_2$. Calculated (%): C, 45.50; H, 4.86. ^{1}H NMR (CD_3COCD_3), δ: 2.27, 3.17, 3.20 (all s, 3 H each, CH_3CO, 2 SO_2CH_3); 4.49 (s, 2 H, CH_2); 7.93 (d, 1 H, J = 1.9 Hz); 8.09 (dd, 1 H, J = 8.3 Hz, J = 1.9 Hz); 7.49 (d, 1 H, J = 8.3 Hz). ^{13}C NMR (CD_3COCD_3), δ: 19.9, 33.3, 33.9, 37.4, 111.7, 120.9, 122.1, 126.8, 133.6, 134.9, 194.7.

1-[2-Methyl-3,6-bis(methylsulfonyl)phenyl]acetone (4g). The yield was 93%, colorless crystals, m.p. 221 °C. Found (%): C, 47.01; H, 4.99. $C_{12}H_{16}O_5S_2$. Calculated (%): C, 47.35; H, 5.30. ^{1}H NMR (CD_3COCD_3), δ: 2.32, 2.64, 3.17, 3.25 (all s, 3 H each, CH_3, CH_3CO, 2 SO_2CH_3); 4.58 (s, 2 H, CH_2); 8.11, 8.17 (both d, 1 H each, J = 8.2 Hz). ^{13}C NMR (DMSO-d_6), δ: 15.9, 29.7, 43.2, 43.7, 43.8, 126.8, 127.6, 136.7, 139.6, 143.9, 134.9, 203.9.

Reactions of thiophene 1,1-dioxides 1b,g with methyl furan-2-carboxylate (5c) (general procedure). A solution of thiophene dioxide (1 mmol) and ester **5c** (1.1 mmol) in tetrachloroethylene (10 mL) was rapidly heated to 100 °C. The workup described above for compounds **4a—g** gave esters **6a,b**. When the reaction mixture was refluxed at ~120 °C prior to workup, esters **7a,b** were obtained.

Methyl 7-chloro-4-methylsulfonyl-3a,7a-dihydro-1-benzofuran-2-carboxylate (6a). The yield was 100%, a light yellow oil. Found (%): C, 45.31; H, 3.79. $C_{11}H_{11}ClO_5S$. Calculated (%): C, 45.44; H, 3.81. ^{1}H NMR ($CDCl_3$), δ: 2.93, 3.77 (both s, 3 H each, CO_2CH_3, SO_2CH_3); 4.43—4.47 (d, 1 H, C(3a)H, J = 13.7 Hz); 5.52 (d, 1 H, C(7a)H, J = 13.7 Hz); 6.23 (d, 1 H, J = 3.1 Hz); 6.36 (d, 1 H, J = 6.9 Hz); 6.81—6.83 (dd, 1 H, J = 1.6 Hz, J = 6.9 Hz). ^{13}C NMR (DMSO-d_6), δ: 40.1, 48.3, 52.0, 118.6, 128.3, 131.9, 136.5, 147.1, 148.9, 161.0.

Methyl 3-(5-chloro-2-methylsulfonylphenyl)-2-hydroxyacrylate (7a). The yield was 87%, a dark oil. Found (%): C, 45.12; H, 3.66. $C_{11}H_{11}ClO_5S$. Calculated (%): C, 45.44; H, 3.81. ^{1}H NMR (DMSO-d_6), δ: 3.20, 3.83 (both s, 3 H each, CO_2CH_3, SO_2CH_3); 7.16 (s, 1 H, CH=C); 7.58—7.61 (m, 1 H, Ar); 7.97 (d, 1 H, Ar, J = 8.4 Hz); 8.34 (d, 1 H, Ar, J = 1.8 Hz); 10.61 (s, 1 H, OH). ^{13}C NMR (DMSO-d_6), δ: 45.4, 51.5, 118.0, 129.7, 130.6, 130.9, 139.8, 140.0, 145.1, 163.9.

Methyl 4,7-bis(methylsulfonyl)-3a,7a-dihydro-1-benzofuran-2-carboxylate (6b). The yield was 100%, a yellow oil. Found (%): C, 43.13; H, 4.36. $C_{12}H_{14}O_7S_2$. Calculated (%): C, 43.10; H, 4.22. ^{1}H NMR (DMSO-d_6), δ: 3.23, 3.29, 3.71 (all s, 3 H each, 2 SO_2CH_3, CO_2CH_3); 4.51—4.53 (d, 1 H, C(3a)H, J = 13.9 Hz); 5.52 (d, 1 H, C(7a)H, J = 13.9 Hz); 6.35, 6.39 (both d, 1 H each, J = 3.3 Hz, J = 7.1 Hz); 6.85—6.87 (dd, 1 H, J = 1.8 Hz, J = 7.1 Hz). ^{13}C NMR (DMSO-d_6), δ: 40.9, 48.5, 52.8, 119.1, 129.1, 132.5, 137.0, 147.9, 149.4, 163.5.

Methyl 3-[2,5-bis(methylsulfonyl)phenyl]-2-hydroxyacrylate (7b). The yield was 90%, colorless crystals, m.p. 211 °C. Found (%): C, 43.20; H, 4.14. $C_{12}H_{14}O_7S_2$. Calculated (%): C, 43.10; H, 4.22. ^{1}H NMR (DMSO-d_6), δ: 3.06, 3.83, 3.89 (all s, 3 H each, CO_2CH_3, 2 SO_2CH_3); 7.22 (s, 1 H, CH=C); 7.63—7.65 (m, 1 H, Ar); 8.09 (d, 1 H, Ar, J = 8.6 Hz); 8.38 (d, 1 H, Ar, J = 2.0 Hz); 11.23 (s, 1 H, OH). ^{13}C NMR (DMSO-d_6), δ: 45.9, 52.0, 119.1, 130.1, 132.8, 133.7, 140.5, 141.9, 146.0, 165.4.

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