Competition between Hetero-*Diels-Alder* and Cheletropic Additions of Sulfur Dioxide to 2-Substituted Buta-1,3-dienes. Synthesis of 2-(1-Naphthyl)- and 2-(2-Naphthyl)buta-1,3-diene

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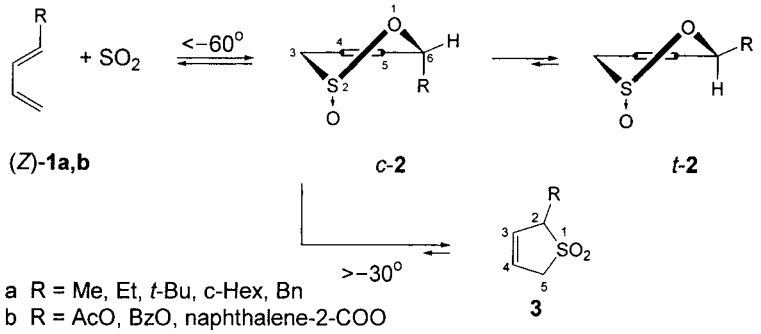
Chloroprene (=2-chlorobuta-1,3-diene; **4b**) and electron-rich dienes such as 2-methoxy-(**4c**), 2-acetoxy-(**4d**), and 2-(phenylseleno)buta-1,3-diene (**4e**) refused to equilibrate with the corresponding sultines **5** or **6** between – 80 and – 10° in the presence of excess SO_2 and an acidic promoter. Isoprene (**4a**) and 2-(triethylsilyl)-(**4f**), 2-phenyl-(**4g**), and 2-(2-naphthyl)buta-1,3-diene (**4i**) underwent the hetero-*Diels-Alder* additions with SO_2 at low temperature. In contrast, 2-(1-naphthyl)buta-1,2-diene (**4h**) did not. With dienes **4a**, **4g**, and **4i**, the hetero-*Diels-Alder* additions with SO_2 gave the corresponding 4-substituted sultine **5** with high regioselectivity. In the case of **4g** + SO_2 ⇄ **5g**, the energy barrier for isomerization of **5g** to 5-phenylsultine (**6g**) was similar to that of the cheletropic addition of **4g** to give 3-phenylsulfolene (**7g**). The hetero-*Diels-Alder* addition of **4f** gave a 1:4 mixture of the 4-(triethylsilyl)sultine (**5f**) and 5-(triethylsilyl)sultine (**6f**). The preparation of the two new dienes **4h** and **4i** is reported.

Introduction. – In the two preceding reports [1][2], we have demonstrated that the competition between hetero-*Diels-Alder* and cheletropic additions of sulfur dioxide depends strongly on the nature of the conjugated dienes. At low temperature (– 80°) and in the presence of an acidic promoter, SO_2 adds to (*E*)-1-alkylbuta-1,3-diene (*E*)-**1a** giving, in agreement with the *endo Alder* rule [2], the corresponding *cis*-6-alkyl-2,6-dihydro-1,2-oxathiin 2-oxides (*cis*-sultines *c*-**2a**), which then equilibrate with their more stable *trans*-isomers (*trans*-sultines *t*-**2a**) (*Scheme 1*).

Scheme 1



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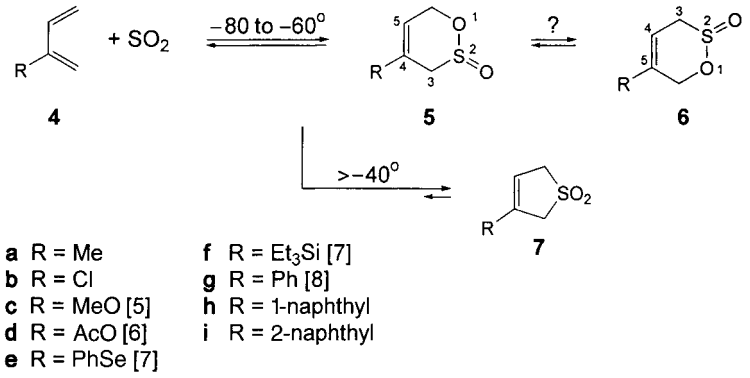
The hetero-*Diels-Alder* additions of 1,2-dimethylidenecycloalkanes [1] and of (*E*)-ethylidene-2-methylidenecyclohexane [2] are fast reactions at $-80°$ without acid catalysis. In the case of (*E*)-1-(acyloxy)buta-1,3-dienes (*E*)-**1b**, 1:10 mixtures of the corresponding *cis*- and *trans*-6-(acyloxy)sultines **2b** are formed slowly with an excess of SO_2 premixed with CF_3COOH. In all cases, the hetero-*Diels-Alder* additions of SO_2 to (*E*)-1-alkyl- and (*E*)-1-(acyloxy)buta-1,3-dienes are highly regioselective, giving exclusively the corresponding 6-substituted sultines; no regioisomeric 3-substituted sultines can be detected before formation of the corresponding 2-substituted 2,5-dihydrothiophene 1,1-dioxides (=sulfolenes) **3** (*Scheme 1*). (*Z*)-1-Alkyl- and (*Z*)-1-(acyloxy)buta-1,3-dienes do not undergo the hetero-*Diels-Alder* additions with SO_2. Strikingly, 1-substituted buta-1,3-dienes more electron-rich than (*E*)-1-alkyl- and (*E*)-1-(acyloxy)buta-1,3-dienes refuse to equilibrate with the corresponding sultines between $-100°$ and $10°$, with or without acidic promoter. These dienes include 1-phenyl-, 1-(4-methoxyphenyl)-, 1-cyclopropyl-, 1-(trimethylsilyl)-, 1-methoxy-, 1-(aryloxy)-, 1-(methylthio)-, 1-(arylthio)-, 1-(phenylseleno)- [2], 1-(silyloxy)-, and 1-(alkyloxy)buta-1,3-dienes [3]. In a preliminary report [4], we have shown that isoprene (**4a**) adds to SO_2 in the hetero-*Diels-Alder* mode in the presence of a protic or *Lewis* acid catalyst. The reaction is highly regioselective, giving exclusively 4-methylsultine (**5a**).

We now repeated this latter experiment and reacted isoprene (**4a**) with excess SO_2 (5–20 fold) and 1 equiv. of CF_3COOH or $BF_3 \cdot Et_2O$ for several days at $-60°$ (K(**4a** + $SO_2 \rightleftarrows$ **5a**) ≈ 0.03 lmol^{-1}). No trace of the isomeric sultine **6a** could be detected before or during the slow formation of 3-methylsulfolene (**7a**) (*Scheme 2*). This suggested that the hetero-*Diels-Alder* addition **4a** + $SO_2 \rightleftarrows$ **6a** has an energy barrier higher than that of the cheletropic addition **4a** + $SO_2 \rightarrow$ **7a**. To learn more about the hetero-*Diels-Alder* reactivity of sulfur dioxide, we explored the reactions of the known 2-substituted buta-1,3-dienes **4b**–**g** [5–8] (*Scheme 2*). As we shall see, 2-chloro- (**4b**), 2-methoxy- (**4c**), 2-(acyloxy)- (**4d**), and 2-(phenylseleno)buta-1,3-diene (**4e**) refused to add to SO_2 in the hetero-*Diels-Alder* mode. Contrary to (*E*)-1-(trimethylsilyl)buta-1,3-diene, which did not equilibrate with the corresponding 6-substituted sultine in the presence of excess SO_2 and an acid promoter, 2-(triethylsilyl)buta-1,3-diene (**4f**) generated a mixture of 4- and 5-(triethylsilyl)sultine during reaction with SO_2 at low temperature. Similarly, although (*E*)-1-phenyl- and (*E*)-1-(4-methoxyphenyl)buta-1,3-dienes refused to generate the corresponding sultines with SO_2 2-phenylbuta-1,3-diene (**4g**) underwent a regioselective hetero-*Diels-Alder* addition with SO_2, giving first 4-phenylsultine **5g**, which then equilibrated with the regioisomeric adduct **6g** concurrently with the formation of the more stable 3-phenylsulfolene (**7g**) [9]. This interesting result led us to explore the reactivity of SO_2 with other 2-aryl-substituted butadienes. With this goal in mind, we prepared two unknown dienes 2-(1-naphthyl)buta-1,3-diene (**4h**) and 2-(2-naphthyl)buta-1,3-diene (**4i**) and studied their reactivity toward SO_2. While **4h** refused to equilibrate with the expected sultines **5h** and **6h**, **4i** reacted with SO_2 in the presence of CF_3COOH, giving sultine **5i** exclusively. No trace of isomeric sultine **6i** could be seen prior to its isomerization to sulfolene **7i**.

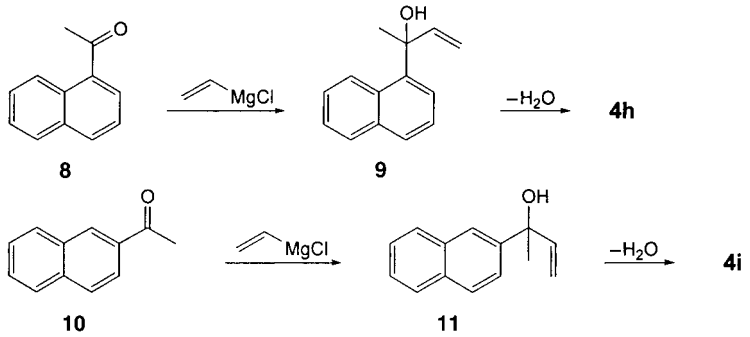
Syntheses of the New Dienes. – Dehydration of 2-(1-naphthyl)but-3-en-1-ol (**9**; obtained in 70% yield by addition of vinylmagnesium chloride to 1-acetonaphthone

Scheme 2



(**8**)) promoted by a catalytic amount of aniline hydrobromide afforded 2-(1-naphthyl)buta-1,3-diene (**4h**) in 23% yield (*Scheme 3*). Similarly, 2-(2-naphthyl)buta-1,3-diene (**4i**) was obtained in 17% yield by H_2O elimination from 2-(2-naphthyl)but-3-en-1-ol (**11**) derived from 2-acetonaphthone (**10**).

Scheme 3



Reactions with Sulfur Dioxide. – As already reported [10], chloroprene (=2-chlorobuta-1,3-diene; **4b**) underwent cheletropic addition with SO_2, giving sulfolene **7b** at 25–50°. No trace of isomeric sultines **5b** or/and **6b** could be detected after prolonged exposure to a large excess of SO_2 and 1 equiv. of CF_3COOH at −100° up to 20°. We attribute this lack of hetero-*Diels-Alder* reactivity of chloroprene (**4b**) compared with isoprene (**4a**) [4] to the electron-withdrawing effect of the chloro substituent. Surprisingly, 2-methoxybuta-1,3-diene (**4c**) [5] refused to equilibrate with sultines **5c** or **6c** between −100 and −30° in excess SO_2 without acidic promoter. Above −30°, the known sulfolene **7c** was formed [11]. In the presence of CF_3COOH or $BF_3 \cdot OEt_2$ and SO_2, diene **4c** was rapidly polymerized already at −80°. It appears, therefore, that the electron-rich diene **4c** that is expected to react faster than chloroprene and isoprene in a hetero-*Diels-Alder* addition is not able to equilibrate with sultines **5c** or **6c**. A similar

observation was made when comparing the SO_2 reactivity toward (*E*)-1-methoxybuta-1,3-diene, (*E*)-piperylene (=(*E*)-penta-1,3-diene), and (*E*)-1-chlorobuta-1,3-diene [3a][12]. It is not excluded that the hetero-*Diels-Alder* additions **4c** + SO_2 ⇄ **5c** + **6c** are not exothermic enough for the sultines to exist at equilibrium with the cycloaddents above −100°, this being due to differential solvation by SO_2.

Unlike (*E*)-1-(acyloxy)buta-1,3-diene, which added to SO_2 in the presence of CF_3COOH at −80° in the hetero-*Diels-Alder* mode [2][12], 2-(acyloxy)buta-1,3-diene (**4d**) did not equilibrate with sultines **5d** or/and **6d** in the presence of a large excess of SO_2 and 1 equiv. of CF_3COOH between −80 and 20°. Above 20°, **4d** added in the cheletropic mode, giving the sulfolene **7d**. In the preceding report [2], we have shown that 2-(phenylseleno)buta-1,3-diene (**4e**) generates exclusively sulfolene **7e** when mixed with SO_2, at −30° already. As in the case of **7b**–**d**, no sultine **5e** or **6e** could be observed.

Unlike (*E*)-1-(trimethylsilyl)buta-1,3-diene, which refused to undergo the hetero-*Diels-Alder* addition with SO_2, with or without acidic promoter, 2-(triethylsilyl)buta-1,3-diene (**4f**) [7] equilibrated with a 1:4 mixture of 4-(triethylsilyl)sultine (**5f**) and 5-(triethylsilyl)sultine (**6f**) at −80° in the presence of an excess of SO_2 and 1 equiv. of CF_3COOH. Equilibrium (K(**4f** + SO_2 ⇄ **5f** + **6f**) ≈ 0.069 $lmol^{-1}$) was reached at −80° in 48 h (^{1}H-NMR, toluene as internal reference). Above −50°, both sultines **5f** and **6f** underwent the cycloreversion to diene **4f** + SO_2, and the cheletropic addition giving sulfolene **7f** was complete after a few hours at 25°. The ratio of sultines **5f** and **6f** stayed the same (1:4) from the early stage of their formation at −80° until their cycloreversion at −50°, indicating that these two cycloadditions reach equilibrium or not under these conditions. Both results are consistent with a regioselectivity controlled by the kinetics or the thermodynamics of the hetero-*Diels-Alder* addition. The ^{1}H-NMR data of **5f** and **6f** are summarized in *Fig. 1*. The observations of similar vicinal coupling constants ^3J(6a,5) = 2.7 Hz and ^3J(6e,5) = 3.0 Hz in **5f** suggests that this sultine adopts either an envelope (sofa) conformation *E*-**5f** with the O-atom lying in the plane of the π system [13], or exists as an equilibrium of two pseudo-chairs *C*-**5f** and *C*′-**5f** of similar stabilities. In the case of sultine **6f**, its ^{1}H-NMR spectrum showed different homoallylic coupling constants [14] ^5J(3e,6a) = 2.7 Hz, ^5J(4e,6e) < 1 Hz, ^5J(3a,6e) = 2.7 Hz and ^5J(3a, 6a) = 4.0 Hz as well as different vicinal coupling constants ^3J(3e,4) = 5.8 Hz and ^3J(3a,4) = 2.7 Hz that are consistent with **6f** residing in a major pseudo-chair conformation *C*-**6f** (*Fig. 1*). The structures of the major sultine **6f** was confirmed by its 2D ^{1}H,^{1}H-NOESY data (significant cross-peaks for H_a–C(3) (3.66 ppm)/H–C(4) (6.23 ppm), H_e–C(3) (3.23 ppm)/H–C(4), H_a–C(6) (4.72 ppm)/Et_3Si, and H_e–C(6)/Et_3Si). The pseudo-axial position of the S=O moieties is proposed, as predicted by high-level quantum calculations [12][15].

In the absence of acid promoter, 2-phenylbuta-1,3-diene (**4g**) underwent the hetero-*Diels-Alder* addition with SO_2 at −80° giving small amounts of 4-phenylsultine (**5g**) exclusively. After 15 h at −80°, the conversion of **4g** to **5g** remained less than 5%. Sultine **5g** was stable between −80 and −40°. Above −40°, the concurrent cheletropic addition occurred, giving the known sulfolene **7g** [9] at the expense of **5g**. Complete formation of sulfolene **7g** was observed after a few hours at 25°. In the presence of 1 equiv. of CF_3COOH, 2-phenylbuta-1,3-diene (**4g**) added rapidly to SO_2, giving at −80° sultine **5g** with an equilibrium constant K(**4g** + SO_2 ⇄ **5g**) ≈ 0.55 $lmol^{-1}$ (by

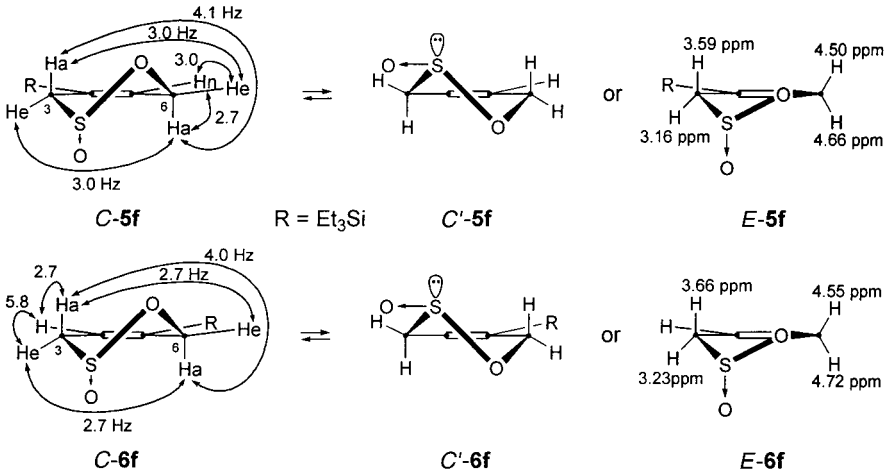


Fig. 1. *Possible conformations adopted by sultines* **5f** *and* **6f** ($R = Et_3Si$)

^{1}H-NMR, toluene as internal reference). Raising the temperature to $-40°$ led to the formation of the regioisomeric sultine **6g** at the expense of **5g**. After 120 h at $-40°$, a 0.13 : 0.08 : 1 mixture of sultine **5g**, sultine **6g**, and sulfolene **7g** was observed. Compared with the hetero-*Diels-Alder* addition of isoprene with SO_2 for which an equilibrium constant $K(\mathbf{4a} + SO_2 \rightleftarrows \mathbf{5a}) = 0.053$ lmol^{-1} was measured at $-80°$, equilibrium constant $K(\mathbf{4g} + SO_2 \rightleftarrows \mathbf{5g})$ is 10 times larger. One might attribute this observation to the π conjugation of the phenyl substituent that makes sultines **5g** and **6g** more electron-rich than sultine **5a**, and thus more prone to specific solvation by SO_2 (charge-transfer-complex formation? [2]). The structures of sultines **5g** and **6g** were inferred from their ^{1}H-NMR (*Fig. 2*) and 2D ^{1}H,^{1}H-NOESY data.

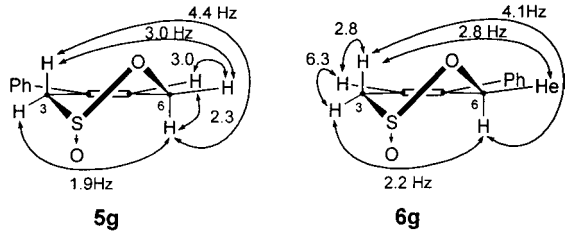


Fig. 2. *Most probable conformations for sultines* **5g** *and* **6g**

Under conditions of kinetic control, the regioselectivity of the hetero-*Diels-Alder* addition of 2-phenylbuta-1,3-diene (**4g**) to SO_2 was the same as that observed with isoprene [4]. Both sultines **5g** and **6g** appear to have similar stabilities in SO_2. The isomerization **5g** $\rightleftarrows$ **6g** has an energy barrier similar to that of the sultine $\rightarrow$ sulfolene isomerization **5g** + **6g** $\rightarrow$ **7g**, which makes 2-phenylbuta-1,3-diene (**4g**) different from isoprene (**4a**) in its reactivity toward SO_2. Both sultines **5g** and **6g** seem to prefer pseudo-chair conformations (*Fig. 2*), as indicated by the vicinal and homoallylic coupling constants.

The 2-(1-naphthyl)buta-1,3-diene (**4h**) underwent the cheletropic addition to SO_2 above $-30°$, giving sulfolene **7h**. No hetero-*Diels-Alder* addition could be observed between -80 and $25°$ in the presence of a large excess of SO_2 with or without acid promoter (CF_3COOH, $BF_3 \cdot Et_2O$). In contrast, 2-(2-naphthyl)buta-1,3-diene (**4i**) underwent a regioselective hetero-*Diels-Alder* addition of SO_2 at $-80°$ in the presence of CF_3COOH, affording sultine **5i**. Above $-50°$, sultine **5i** underwent the cycloreversion into diene **4i** and SO_2, which then reacted in the cheletropic mode giving sulfolene **7i**. Sultine **5i** could not be isomerized to its regioisomer **6i**, in contrast with the behavior of the phenyl-substituted derivative **5g** that was isomerized to **6g** and **7g** competitively. The ^{1}H-NMR data of sultine **5i** suggest a preferred pseudo-chair conformation analogous to that shown in *Fig. 2* for **5g** ($^3J(5,6a) = 3.3$ Hz, $^3J(5,6a) = 2.4$ Hz, $^5J(3e,6a) = 2.4$ Hz, $^5J(3a,6e) = 3.3$ Hz, $^5J(3a,6a) = 4.4$ Hz).

The inability of 2-(1-naphthyl)buta-1,3-diene (**4h**) to add to SO_2 in the hetero-*Diels-Alder* mode can be assigned to its ground-state conformation that avoids conjugation between the naphthalene and butadiene units for steric reasons. Indeed, for an easy cycloaddition, the 1-naphthyl group should be coplanar with the *s-cis*-butadiene moiety. Severe steric-repulsion interactions between these groups make these conformations too unstable. This phenomenon is less severe for the *s-cis* forms of 2-(2-naphthyl)buta-1,3-diene (**4i**) as shown in *Fig. 3*). Diene **4i** is more like 2-phenylbuta-1,3-diene than **4h**.

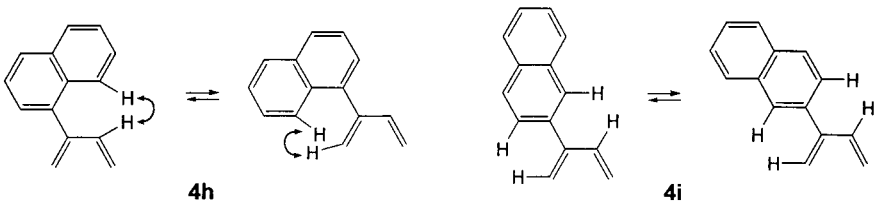
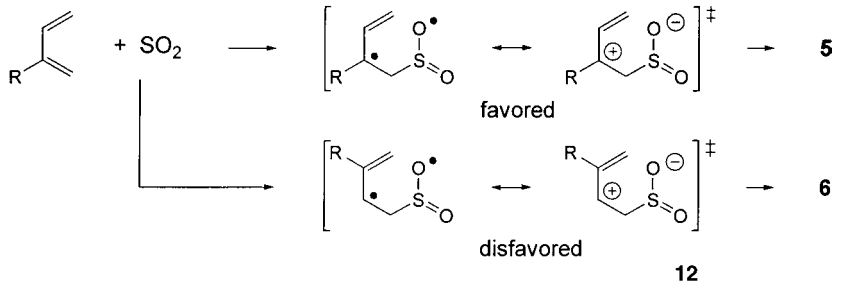


Fig. 3. *Difference in back-strain for the planar conformers of* s-cis *butadienes* **4h** *and* **4i**

The Regioselectivity of the Hetero-*Diels-Alder* Additions of Sulfur Dioxide. – The PMO theory [16][17] predicts that the hetero-*Diels-Alder* additions of SO_2 to 2-substituted buta-1,3-dienes **4** should be regioselective under conditions of kinetic control and give preferentially the corresponding 4-substituted sultines **5**, as observed for the reactions of isoprene (**4a**) [4], 2-(triethylsilyl)buta-1,3-diene (**4f**), and 2-arylbuta-1,3-dienes **4g** and **4i**. The theory of the diradicaloids [18] leads to the same prediction if one assumes the C–S bond of the sultines formed earlier than the C–O bond in the transition states. This hypothesis will be confirmed by deuterium kinetic and thermodynamic isotope effects [19]. Accordingly (*Scheme 4*), the hetero-*Diels-Alder* addition **4f** + SO_2 → **5f** should be preferred over **4f** + SO_2 → **6f** under conditions of kinetic control as the stabilizing β-silyl effect [20] cannot operate for reasons of geometry (no hyperconjugation 2p(+)/C–Si) in the zwitterionic limiting structure **12**. The observation that sultine **6f** is formed preferentially (sultine **5f**/**6f** ratio of 1:4) suggests, therefore, that the regioselectivity of that hetero-*Diels-Alder* addition is governed by the stability difference between the two sultines **5f** and **6f**, rather than by kinetic control.

Scheme 4



The model of the diradicaloids of the transition structures of the hetero-*Diels-Alder* additions of SO_2 predicts also that these reactions are catalyzed by *Broenstedt* and *Lewis* acids, as observed, and as predicted also by high-level quantum calculations of these reaction hypersurfaces [12][15]. It can be applied to predict the regioselectivity of the hetero-*Diels-Alder* additions of SO_2 to 1-substituted buta-1,3-dienes. In agreement with experiments [2] and high-level quantum calculations [12][15], these cycloadditions generate 6-substituted sultines, rather than their 3-substituted isomers under conditions of kinetic control.

Conclusions. – In the presence of an acidic promoter, SO_2 added at $-80°$ to 2-phenyl-(**4g**) and 2-(2-naphthyl)buta-1,3-diene (**4i**) giving the corresponding 4-substituted sultines **5g** and **5i**, respectively. The regioselectivity was the same as for the hetero-*Diels-Alder* addition of isoprene (**4a**) to SO_2 that gave 4-methylsultine (**5a**), which could not be equilibrated with its 3-methyl isomer **6a** after staying at $-60°$. In contrast, 4-phenylsultine (**5g**) was isomerized to 5-phenylsultine (**6g**) concomitantly with the cheletropic addition, providing the more stable 3-phenylsulfolene (**7g**). In the case of the addition of SO_2 to 2-(2-naphthyl)buta-1,3-diene (**4i**), 5-(2-naphthyl)sultine (**5i**) was formed at $-80°$. It could not be isomerized to its sultine **6i** before the formation of the corresponding sulfolene **7i**. At $-80°$ and in the presence of CF_3COOH, 2-(triethylsilyl)buta-1,3-diene (**4f**) added to SO_2 in the hetero-*Diels-Alder* mode giving a 1:4 mixture of 4-(triethylsilyl)- (**5f**) and 5-(triethylsilyl)sultine (**6f**); their ratio did not change until their conversion into 3-(triethylsilyl)sulfolene (**7f**). Finally, we found that 2-(1-naphthyl)buta-1,3-diene (**4h**) refused to equilibrate with the expected sultine **5h** or **6h**, probably for reasons of back-strain in its planar *s-cis* conformation.

Chloroprene (**4b**) refused also to undergo the hetero-*Diels-Alder* addition with SO_2, as did the more electron-rich dienes such as 2-methoxy-(**4c**), 2-acetoxy-(**4d**), and 2-(phenylseleno)buta-1,3-diene (**4e**). The regioselectivity of the hetero-*Diels-Alder* additions of SO_2 under kinetic control can be predicted by the diradicaloid model, assuming that the C–S bonds in sultines are formed earlier than the C–O bonds. Differential solvation effects are probably the cause of the failure to observe sultines with the most-electron-rich dienes. The competition between hetero-*Diels-Alder* and cheletropic additions of 2-substituted buta-1,3-dienes is, or is not, parallel with that observed with 1-substituted buta-1,3-dienes, depending on the nature of the substituent.

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Experimental Part

General. See [2][12][21].

2-(Naphthalen-1-yl)buta-1,3-diene (**4h**). A mixture of **10** (1 g, 5 mmol), aniline hydrobromide (69 mg, 0.43 mmol), and hydroquinone (24 mg, 0.21 mmol) was heated to 130° in a flask connected to a *Vigreux* column under reduced pressure (0.1 mbar). The yellowish oil collected in the receiver was purified by FC (CH_2Cl_2): 200 mg (23%) of **4h**. Colorless oil. UV (MeCN): 280 (7400), 228 (12200). IR (film): 3045, 1815, 1590, 1505, 1405, 1255, 990, 905, 780, 660. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.91 (*m*, 3 arom. H); 7.43 (*m*, 3 arom. H); 7.37 (*m*, arom. H); 6.81 (*dd*, ^3J(3,4) = 17.3, ^3J(3,4) = 10.4, H−C(3)); 5.63 (*m*, H_a−C(1)); 5.30 (*m*, H_b−C(1)); 5.16 (*dm*, ^3J(3,4) = 10.4, H_a−C(4)); 4.74 (*dm*, ^3J(3,4) = 17.3, H_b−C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 147.4 (*s*, C(2)); 139.1 (*d*, ^1J(C,H) = 155, C(3)); 137.7, 133.5, 131.8 (3*s*); 128.1 (*d*, ^1J(C,H) = 158, arom. C); 127.6 (*d*, ^1J(C,H) = 158, arom. C); 126.6 (*d*, ^1J(C,H) = 161, arom. C); 126.3 (*d*, ^1J(C,H) = 160, arom. C); 125.7 (*d*, ^1J(C,H) = 160, arom. C); 125.6 (*d*, ^1J(C,H) = 160, arom. C); 125.3 (*d*, ^1J(C,H) = 160, arom. C); 117.7 (*t*, ^1J(C,H) = 158, C(1)); 119.6 (*t*, ^1J(C,H) = 160, C(4)). CI-MS (NH_3): 181 (100, $[M+1]^+$), 165 (84), 152 (20), 126 (21), 115 (36), 89 (55). Anal. calc. for $C_{14}H_{12}$ (180.24): C 93.29, H 6.71; found: C 93.25, H 6.63.

2-(Naphthalen-2-yl)buta-1,3-diene (**4i**). As described for **4h**, with **12** (6.7 g, 34 mmol): 600 mg (17%) of **4i**. Colorless oil. UV (MeCN): 224 (18800). IR (film): 3055, 1740, 1585, 1505, 990, 895, 860, 750. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.85 (*m*, 4 arom. H); 7.50 (*m*, 3 arom. H); 6.76 (*dd*, ^3J(3,4) = 17.4, 10.7, H−C(3)); 5.44 (*m*, H_a−C(1)); 5.38 (*m*, H−C(1)); 5.31 (*dm*, ^3J(3,4) = 10.7, H_a−C(4)); 5.29 (*dm*, ^3J(3,4) = 17.4, H−C(4)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 148.2 (*s*, C(2)); 138.2 (*d*, ^1J(C,H) = 155, C(3)); 137.2, 133.3, 132.8 (3*s*); 128.0 (*d*, ^1J(C,H) = 160, arom. C); 127.6 (*d*, ^1J(C,H) = 161, arom. C); 127.5 (*d*, ^1J(C,H) = 158, arom. C); 127.0 (*d*, ^1J(C,H) = 159, arom. C); 126.6 (*d*, ^1J(C,H) = 160, arom. C); 126.1 (*d*, ^1J(C,H) = 160, arom. C); 125.9 (*d*, ^1J(C,H) = 160, arom. C); 117.4 (*t*, ^1J(C,H) = 158, C(1)); 117.2 (*t*, ^1J(C,H) = 158, C(4)). CI-MS (NH_3): 181 (100, $[M+1]^+$), 165 (12), 115 (12), 102 (7), 89 (14). Anal. calc. for $C_{14}H_{12}$ (180.24): C 93.29, H 6.71; found: C 93.20, H 6.82.

2-(Naphthalen-1-yl)but-3-en-2-ol (**9**). A soln. of 1-acetonaphthone (= 1-(naphthalen-1-yl)ethanone; **8**; 5 g, 4.5 ml, 29 mmol) in THF (5 ml) was added slowly to a soln. of vinylmagnesium chloride (1.7M in THF; 20.6 ml, 35 mmol) under N_2. The mixture was stirred at 80° for 1 h, then sat. aq. NH_4Cl soln. (15 ml) was added at 25°. The mixture was extracted with AcOEt (3 × 15 ml) and the combined org. phase dried ($MgSO_4$) and evaporated. FC (CH_2Cl_2): 4 g (70%) of **9**. Colorless oil. UV (MeCN): 279 (26200), 270 (22600). IR (film): 3415, 3050, 2980, 1510, 1370, 1110, 925, 805, 780, 730. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.56 (*m*, arom. H); 7.89 (*m*, arom. H); 7.83 (*m*, arom. H); 7.73 (*m*, arom. H); 7.49 (*m*, 3 arom. H); 6.43 (*dd*, ^3J(3,4) = 17.4, 10.7, H−C(3)); 5.31 (*dd*, ^2J = 1.0, ^3J(3,4) = 17.4, H−C(4)); 5.25 (*dd*, ^2J = 1.0, ^3J(3,4) = 10.7, H−C(4)); 2.30 (OH); 1.92 (*s*, Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 145.2 (*d*, ^1J(C,H) = 155, C(3)); 141.2, 134.7, 130.6 (3*s*); 128.8 (*d*, ^1J(C,H) = 160, arom. C); 128.7 (*d*, ^1J(C,H) = 160, arom. C); 127.4 (*d*, ^1J(C,H) = 159, arom. C); 125.1 (*d*, ^1J(C,H) = 160, arom. C); 124.8 (*d*, ^1J(C,H) = 159, arom. C); 123.5 (*d*, ^1J(C,H) = 160, arom. C); 113.6 (*t*, ^1J(C,H) = 156, C(4)); 75.7 (*s*, C(2)); 29.7 (*q*, ^1J(C,H) = 128, Me). CI-MS (NH_3): 198 (100, $M^{+\cdot}$), 181 (88), 165 (12), 141 (7), 115 (3). Anal. calc. for $C_{14}H_{14}O$ (198.26): C 84.81, H 7.12; found: C 84.70, H 7.17.

2-(Naphthalen-2-yl)but-3-en-2-ol (**11**). As described for **9**, with 2-acetonaphthone (= 1-(naphthalen-2-yl)ethanone; **10**; 5 g, 4.5 ml, 29 mmol) in THF (5 ml): 4 g (70%) of **11**. Colorless oil. UV (MeCN): 226 (9500). IR (film): 3395, 3055, 2980, 1600, 1505, 1370, 1125, 925, 860, 820, 750. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.97 (*m*, arom. H); 7.86 (*m*, 3 arom. H); 7.59 (*m*, arom. H); 7.49 (*m*, 2 arom. H); 6.28 (*dd*, ^3J(3,4) = 9.2, ^3J(3,4) = 15.0, H−C(3)); 5.36 (*dd*, ^2J = 0.9, ^3J(3,4) = 15.0, H−C(4)); 5.25 (*dd*, ^2J = 0.9, ^3J(3,4) = 9.2, H−C(4)); 1.80 (*s*, Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 114.7 (*d*, ^1J(C,H) = 159, C(3)); 143.7, 133.1, 132.4 (3*s*); 127.8 (*d*, ^1J(C,H) = 158, arom. C); 127.4 (*d*, ^1J(C,H) = 158, arom. C); 126.0 (*d*, ^1J(C,H) = 160, arom. C); 125.9 (*d*, ^1J(C,H) = 160, arom. C); 125.8 (*d*, ^1J(C,H) = 160, arom. C); 124.1 (*d*, ^1J(C,H) = 158, arom. C); 123.3 (*d*, ^1J(C,H) = 158, arom. C); 112.7 (*t*, ^1J(C,H) = 156, C(4)); 74.8 (*s*, C(2)); 29.2 (*q*, ^1J(C,H) = 127, CH_3). CI-MS (NH_3): 198 (100, $M^{+\cdot}$), 181 (93), 128 (38), 116 (27), 102 (38).

1:4 Mixture of 3,6-Dihydro-4-(triethylsilyl)-1,2-oxathiin 2-Oxide (**5f**) *and 3,6-Dihydro-5-(triethylsilyl)-1,2-oxathiin 2-Oxide* (**6f**). In a 5-mm NMR tube and in the presence of CF_3COOH (20 mg, 0.18 mmol), 2-(triethylsilyl)buta-1,3-diene (**4f**) [7] (30 mg, 0.18 mmol) reacted with SO_2 (0.3 ml) in CD_2Cl_2 (0.2 ml) at −80° to

give **5f**/**6f** 1:4. This ratio did not change on rising the temp. to $-50°$. At $-80°$, the equilibrium **4f** + SO_2 → **5f** + **6f** was reached in 48 h, and an equilibrium constant $K \approx 0.07$ mol^{-1} dm^3 was evaluated (toluene as internal ref.).

Data of **6f**: ^{1}H-NMR (400 MHz, CD_2Cl_2/SO_2, 223 K; detected signals): 6.23 (*ddd*, ^3J(3eq,4) = 5.8, ^3J(3ax,4) = 2.7, ^4J(4,6ax) = 2.7, H–C(4)); 4.72 (*dddd*, ^2J = 16.5, ^5J(3ax,6ax) = 4.0, ^4J(4,6ax) = 2.7, ^5J(3eq,6ax) = 2.7, H_{ax}–C(6)); 4.55 (*dm*, ^2J = 16.5, H_{eq}–C(6)); 3.66 (*dddd*, ^2J = 17.6, ^5J(3ax,6ax) = 4.0, ^5J(3ax,6eq) = 2.7, ^3J(3ax,4) = 2.7, H_{ax}–C(3)); 3.23 (*ddd*, ^2J = 17.6, ^3J(3eq,4) = 5.8, ^5J(3eq,6ax) = 2.7, H_{eq}–C(3)). ^{13}C-NMR (100.6 MHz, $CD_2Cl_2/CFCl_3/SO_2$, 233 K; detected signals): 146.1 (*s*, C(5)); 121.7 (*d*, ^1J(C,H) = 169, C(4)); 61.2 (*d*, ^1J(C,H) = 154, C(6)); 45.8 (*t*, ^1J(C,H) = 146, C(3)); 6.51 (*q*, 3 C, Me); 1.6 (*t*, 3 C, CH_2).

Data of **5f**: ^{1}H-NMR (400 MHz, CD_2Cl_2/SO_2, 223 K; detected signals): 6.23 (*ddd*, ^3J(5,6eq) = 3.0, ^4J(3ax,5) = 2.7, ^3J(5,6ax) = 2.7, H–C(5)); 4.66 (*dddd*, ^2J = 17.1, ^5J(6ax,3ax) = 4.1, ^5J(3eq,6ax) = 3.0, ^3J(5,6ax) = 2.7, H_{ax}–C(6)); 4.50 (*ddd*, ^2J = 17.1, ^3J(5,6eq) = 3.0, ^5J(3ax,6eq) = 3.0, H_{eq}–C(6)); 3.59 (*dddd*, ^2J = 17.3, ^5J(3ax,6ax) = 4.1, ^5J(3ax,6eq) = 3.0, ^4J(3ax,5) = 2.7,H_{ax}–C(3)); 3.16 (*dd*, ^2J = 17.3, ^5J(3eq,6ax) = 3.0, H_{eq}–C(3)). ^{13}C-NMR (100.6 MHz, $CD_2Cl_2/CFCl_3/SO_2$, 223 K; detected signals): 139.2 (*s*, C(4)); 132.7 (*d*, ^1J(C,H) = 163, C(5)); 58.8 (*t*, ^1J(C,H) = 142, C(6)); 47.1 (*t*, ^1J(C,H) = 149, C(3)).

2,5-Dihydro-3-(triethylsilyl)-thiophene 1,1-Dioxide (**7f**). A mixture of **4f** [7] (40 mg, 0.24 mmol) and SO_2 (*ca*. 0.2 ml, 4–6 mmol) was placed in a *Pyrex* tube and degassed on the vac. line. After sealing the tube under vacuum, the mixture was left at 25° for 12 h. After cooling in liq. N_2, the tube was opened and SO_2 evaporated. The residue was purified. FC (CH_2Cl_2): 42 mg (75%) of **7f**. Colorless oil. UV (MeCN): 206 (2850). IR (film): 2910, 2875, 1585, 1415, 1400, 1310, 1230, 1125, 1035, 1010, 730, 690. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.21 (*m*, H–C(4)); 3.79 (*m*, CH_2(5), CH_2(2)); 0.98 (*t*, ^3J = 8.5, 3 *Me*CH_2); 0.67 (*q*, ^3J = 8.5, 3 Me*CH*).^{13}C-NMR (100.6 MHz, $CDCl_3$): 138.8 (*s*, C(3)); 132.3 (*d*, ^1J(C,H) = 172, C(4)); 58.7 (*t*, ^1J(C,H) = 143, CH_2); 56.5 (*t*, ^1J(C,H) = 134, CH_2); 7.0 (*q*, ^1J(C,H) = 126, *Me*CH_2); 0.7 (*t*, ^1J(C,H) = 118, MeCH_2). ^{17}O-NMR (54 MHz, $CDCl_3$): 164. CI-MS (NH_3): 250 (100, $[M+18]^+$), 233 (7, $[M+1]^+$), 156 (71), 139 (43), 102 (75), 83 (35). Anal. calc. for $C_{10}h_{20}O_2SSi$ (232.41): C 51.68, H 8.67; found: C 51.53, H 8.51.

Mixture of (±)-3,6-Dihydro-5-phenyl-1,2-oxathiin 2-Oxide (**5g**) *and (±)-3,6-Dihydro-4-phenyl-1,2-oxathiin 2-Oxide* (**6g**). As described for **5f**/**6f**, with 2-phenylbuta-1,3-diene (**4g**) [8]. At $-80°$, the equilibrium **4g** + SO_2 ⇄ **5g** was reached in *ca*. 48 h with an equilibrium constant $K \approx 0.55$ mol^{-1} dm^3 (toluene as internal ref.). After 120 h at $-40°$, **4g** was partially converted into **7g**/**5g**/**6g** 1:0.13:0.08.

Data of **5g**: ^{1}H-NMR (400 MHz, CD_2Cl_2/SO_2, 193 K): 7.58 (*m*, 5 arom. H); 6.21 (*ddd*, ^3J(5,6eq) = 3.0, ^4J(3ax,5) = 2.6,^3J(5,6ax) = 2.3, H–C(5)); 4.73 (*dddd*, ^2J = 17.4, ^5J(3ax,6ax) = 4.4, ^3J(5,6ax) = 2.3, ^5J(3eq,6ax) = 1.9, H_{ax}–C(6)); 4.67 (*ddd*, ^2J = 17.4, ^3J(5,6eq) = 3.0, ^5J(3ax,6eq) = 3.0, H_{eq}–C(6)); 3.83 (*dddd*, ^2J = 16.8, ^5J(3ax,6ax) = 4.4, ^5J(3ax,6eq) = 3.0, ^4J(3ax,5) = 2.6, H_{ax}–C(3)); 3.43 (*dd*, ^2J = 16.8, ^5J(3eq,6ax) = 1.9, H_{eq}–C(3)). ^{13}C-NMR (100.6 MHz, $CD_2Cl_2/CFCl_3/SO_2$, 193 K): 139.4 (*s*, 1 C); 128.9 (*d*, ^1J(C,H) = 162, arom. C); 128.8 (*d*, ^1J(C,H) = 161, 2 arom. C); 126.2 (*d*, ^1J(C,H) = 159, 2 arom. C); 124.5 (*s*, 1 C); 120.5 (*d*, ^1J(C,H) = 159, C(5)); 60.4 (*t*, ^1J(C,H) = 153, C(6)); 47.4 (*t*, ^1J(C,H) = 140, C(3)).

Data of **6g**: ^{1}H-NMR (400 MHz, CD_2Cl_2/SO_2, 233 K): 7.50–7.10 (*m*, 5 arom. H); 6.08 (*dddd*, ^3J(3eq,4) = 6.3, ^3J(3ax,4) = 2.8, ^4J(4,6ax) = 2.4, ^4J(4,6eq) = 1.8, H–C(4)); 5.00 (*dddd*, ^2J = 16.1, ^5J(3ax,6ax) = 4.1, ^4J(4,6ax) = 2.4, ^5J(3eq,6ax) = 2.2, H_{ax}–C(6)); 4.90 (*dm*, ^2J = 16.1, H_{eq}–C(6)); 3.83 (*dddd*, ^2J = 17.7, ^5J(3ax,6ax) = 4.1, ^5J(3ax,6eq) = 2.8, ^3J(3ax,4) = 2.8, H_{ax}–C(3)); 3.44 (*ddd*, ^2J = 17.7, ^3J(3eq,4) = 6.3, ^5J(3eq,6ax) = 2.2, H_{eq}–C(3)). ^{13}C-NMR (100.6 MHz, $CD_2Cl_2/CFCl_3/SO_2$, 233 K; detected signals): 111.5 (C(4)); 59.8 (C(6)); 47.3 (C(3)).

2,5-Dihydro-3-phenylthiophene 1,1-Dioxide (**7g**). As described for **7f**, with 2-phenylbuta-1,3-diene (**4g**) [8] (40 mg, 0.30 mmol): 41 mg (68%) of **7g**. White solid. M.p. 123–124°. UV (MeCN): 246 (24700), 208 (2500). IR (KBr): 3000, 1495, 1450, 1395, 1300, 1235, 1125, 1005, 1020, 820, 755, 690, 640. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.45–7.39 (*m*, 5 arom. H); 6.41 (*dddd*, ^3J(4,5) = 3.0, 2.9, ^4J(2,4) = 1.6, 1.5, H–C(4)); 4.12 (*ddd*, ^4J(2,4) = 1.6, 1.5, 1.5, CH_2(2)); 4.00 (*ddd*, ^3J(4,5) = 3.0, ^4J(2,5) = 1.6, 1.5, H–C(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 136.1 (*s*); 133.8 (*s*); 129.1 (*d*, ^1J(C,H) = 164, arom. C); 128.8 (*d*, ^1J(C,H) = 161, 2 arom. C); 125.4 (*d*, ^1J(C,H) = 158, 2 arom. C); 117.1 (*d*, ^1J(C,H) = 171, C(4)); 57.6 (*t*, ^1J(C,H) = 144, C(5)); 56.5 (*t*, ^1J(C,H) = 143, C(2)). ^{17}O-NMR (54 MHz, $CDCl_3$): 168. CI-MS (NH_3): 212 (50, $[M+18]^+$), 194 (2, $M^{+\cdot}$), 130 (100), 115 (82), 91 (32), 77 (26). Anal. calc. for $C_{10}H_{10}O_2S$ (194.25): C 61.84, H 5.19; found: C 61.96, H 5.27.

2,5-Dihydrothiophen-3-ol Acetate 1,1-Dioxide (**7d**). As described for **7f**, with buta-1,3-dien-2-ol acetate (**4d**) [6] (0.2 g), acetone (0.8 ml), and SO_2 (14.3 g, 0.2 mol) for 15 days at 25°. FC (CH_2Cl_2): 280 mg (64%) of **7d**. White solid. M.p. 78–79°. UV (MeCN): 245 (800). IR (KBr): 1760, 1665, 1365, 1325, 1250, 1230, 1195, 1120, 1095, 1010, 905, 830, 785, 680, 605, 470, 420. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.75 (*m*, H–C(4)); 3.94 (*m*, CH_2(2)); 3.89 (*m*, CH_2(5)); 2.19 (*s*, Me). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 168.2 (*s*, CO); 142.0 (*s*, C(3)); 108.0 (*d*, ^1J(C,H) = 176, C(4)); 55.8 (*t*, ^1J(C,H) = 136, C(5)); 54.5 (*t*, ^1J(C,H) = 146, C(2)); 20.6 (*q*, ^1J(C,H) = 131,

Me). CI-MS (NH_3): 194 (100, $[M+18]^+$), 177 (2, $[M+1]^+$), 112 (4), 85 (13). Anal. calc. for $C_6H_8O_4S$ (176.19): C 40.90, H 4.58, S 18.20; found: C 40.80, H 4.61, S 18.18.

2,5-Dihydro-3-(naphthalen-1-yl)thiophene 1,1-Dioxide (**7h**). As described for **7f**, with 2-(naphthalen-1-yl)buta-1,3-diene (**4h**; 40 mg, 0.22 mmol) and SO_2 (*ca.* 0.2 ml, 4–6 mmol). FC (CH_2Cl_2): 38 mg (70%) of **7h**. Colorless oil. UV (MeCN): 225 (18000), 200 (10400). IR (film): 3000, 1395, 1305, 1130, 800, 595, 425. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.90 (*m*, 3 arom. H); 7.55 (*m*, 2 arom. H); 7.48 (*m*, arom. H); 7.35 (*m*, arom. H); 6.17 (*dddd*, ^3J(4,5) = 2.9, 2.9, ^4J(2,4) = 2.1, 2.1, H–C(4)); 4.17 (*ddd*, ^4J(2,4) = 2.1, 2.1, ^4J(2,5) = 1.5, CH_2(2)); 4.11 (*ddd*, ^3J(4,5) = 2.9, ^4J(2,5) = 1.5, 1.5, CH_2(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 137.3, 133.7, 133.4, 130.6, (4*s*, arom. C, C(3)); 129.2 (*d*, ^1J(C,H) = 160, arom. C); 128.7 (*d*, ^1J(C,H) = 160, arom. C); 127.0 (*d*, ^1J(C,H) = 161, arom. C); 126.4 (*d*, ^1J(C,H) = 161, arom. C); 125.7 (*d*, ^1J(C,H) = 160, arom. C); 125.2 (*d*, ^1J(C,H) = 159, arom. C); 124.4 (*d*, ^1J(C,H) = 158, arom. C); 122.5 (*d*, ^1J(C,H) = 173, C(4)); 59.1 (*t*, ^1J(C,H) = 144, C(2)); 57.3 (*t*, ^1J(C,H) = 143, C(5)). CI-MS (NH_3): 262 (100, $[M+18]^+$), 194 (32, $M^{+\cdot}$), 180 (32), 165 (20), 152 (5).

3,6-Dihydro-4-(naphthalen-2-yl)-1,2-oxathiin 2-Oxide (**5i**). As described for **5f**/**6f**, with **4i**. ^{1}H-NMR (400 MHz, CD_2Cl_2/SO_2, 193 K): 7.80–7.50 (*m*, 7 arom. H); 6.47 (*ddd*, ^3J(5,6eq) = 3.3, ^4J(3ax,5) = 2.6, ^3J(5,6ax)) = 2.4, H–C(5)); 4.97 (*dddd*, ^2J = 17.4, ^5J(3ax,6ax) = 4.4, ^3J(5,6ax) = 2.4, ^5J(3eq,6ax) = 2.4, H_{ax}–C(6)); 4.85 (*ddd*, ^2J = 17.4, ^3J(5,6eq) = 3.3, ^5J(3ax,6eq) = 3.0, H_{eq}–C(6)); 4.02 (*dddd*, ^2J = 16.7, ^5J(3ax,6ax) = 4.4, ^5J(3ax,6eq) = 3.0, ^4J(3ax,5) = 2.6, H_{ax}–C(3)); 3.73 (*dd*, ^2J = 16.7, ^5J(3eq,6ax) = 2.4, H_{eq}–C(3)). ^{13}C-NMR (100.6 MHz, $CD_2Cl_2/CFCl_3/SO_2$, 193 K): 140–125 (arom. C, C(4)); 122.6 (*d*, ^1J(C,H) = 159, C(5)); 62.7 (*t*, ^1J(C,H) = 154, C(6)); 49.1 (*t*, ^1J(C,H) = 140, C(3)).

2,5-Dihydro-3-(naphthalen-2-yl)thiophene 1,1-Dioxide (**7i**). As described for **7f**, with a mixture of 2-(naphthalen-2-yl)buta-1,3-diene (**4i**; 40 mg, 0.22 mmol) and SO_2 (0.2 ml). FC (CH_2Cl_2): 42 mg (73%) of **7i**: White solid. M.p. 187–188°. UV (MeCN): 284 (13700), 274 (11600), 244 (36300), 208 (14000). IR (KBr): 3055, 1325, 1310, 1130, 815, 600, 475, 435. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.85 (*m*, 3 arom. H); 7.70 (*m*, arom. H); 7.60 (*m*, arom. H); 7.52 (*m*, 2 arom. H); 6.50 (*ddd*, *J* = 5.0, 3.2, 2.0, H–C(4)); 4.29 (*m*, CH_2(2)); 4.10 (*m*, CH_2(5)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 136.2, 133.4, 133.1, 131.1 (4*s*, arom. C, C(3)); 128.8 (*d*, ^1J(C,H) = 163, arom. C); 128.3 (*d*, ^1J(C,H) = 159, arom. C); 127.7 (*d*, ^1J(C,H) = 158, arom. C); 127.0 (*d*, ^1J(C,H) = 160, arom. C); 126.9 (*d*, ^1J(C,H) = 160, arom. C); 125.4 (*d*, ^1J(C,H) = 159, arom. C); 122.3 (*d*, ^1J(C,H) = 158, arom. C); 117.6 (*d*, ^1J(C,H) = 171, C(4)); 57.8 (*t*, ^1J(C,H) = 143, C(2)); 56.7 (*t*, ^1J(C,H) = 142, C(5)). CI-MS (NH_3): 180 (100, $[M-SO_2]^{+\cdot}$), 165 (47), 152 (17), 141 (6), 115 (6), 89 (13).

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