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α-Oxosulfines Part 2:[1] The First Example of *Ortho*-Thioquinone-*S*-Oxides.

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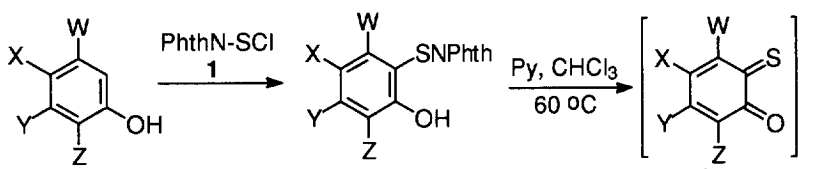
Abstract:. Benzo-oxathiin-*S*-oxides **9b** and **9c** can undergo a Retro Diels-Alder (RDA) reaction to form *ortho*-thioquinone-*S*-oxides **12** and **11**. These hitherto unknown reactive intermediates can be successfully generated as function of the geometry of the starting sulfoxides and the type of aromatic system involved, and can be trapped as electron poor dienes or dienophiles.

We have recently reported[2] that N-arylthiophthalimides can be simply prepared by reacting the phthalimidesulfenyl chloride (PhthN-SCl, Phth = Phthaloyl) **1** with activated arenes and that such compounds can be transformed into aryl thiols or aryl disulfides through simple manipulation of a thiophthalimide residue.[2] When the electrophilic aromatic substitution is performed on hydroxy arenes such as *para*-methoxyphenol **2a**, β-naphthol **2b** and 9-phenanthrol **2c**, the sulfenamides **3a-c** are obtained as single regioisomers. We have also shown that *ortho*-hydroxythiophthalimides **3** react with weak bases, like pyridine, to generate the corresponding *ortho*-thioquinones **4**[3,4] in very mild conditions (SCHEME 1).



2a-c **3a-c** **4a-c**

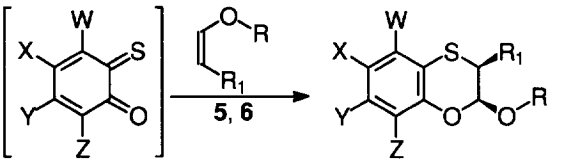
2a, 3a, 4a : W = Y = Z = H ; X = OMe **2b, 3b, 4b** : Y = Z = H ; X, W = Aromatic Ring
2c, 3c, 4c : Y , Z and X, W = Aromatic Ring

SCHEME 1

RESULT AND DISCUSSIONS.

Ortho-thioquionones **4** have been easily trapped as electron poor dienes in inverse electron demand cycloaddition reactions with ethyl vinyl ether **5** or dihydropyran **6** which give benzo-oxathiin derivatives **7a-c** and **8a,b** respectively (SCHEME 2). We became interested in the generation of the hitherto unknown *ortho*-thioquinone-*S*-oxides, using oxathiin-*S*-oxides as starting materials.[1,5] Thus derivatives **7a-c** and **8a,b** were oxidised with *m*-chloroperoxybenzoic acid to the corresponding sulfoxides **9a-c** and **10a,b**. Derivatives **9a-c**

were obtained as *E* and *Z* mixture of diastereoisomers which were separated by flash chromatography, while **10a** and **10b** were the sole products of the oxidation (Figure 1).



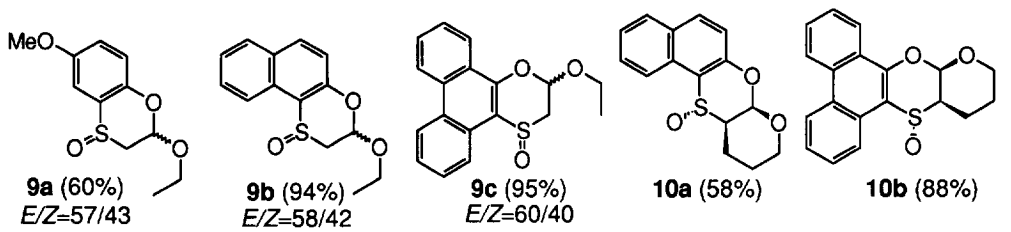
4 a-c **7a-c ; 8a, b**

7a (83%) : W = Y = Z = H ; X = OMe ; R = Et ; R_1 = H
7b (81%) : Y = Z = H ; X, W = Aromatic Ring ; R = Et ; R_1 = H
7c (89%) : Y, Z and X, W = Aromatic Ring ; R = Et ; R_1 = H
8a (84%) : Y = Z = H ; X, W = Aromatic Ring ; R, R_1 = $-(CH_2)_3-$
8b (92%) : Y, Z and X, W = Aromatic Ring ; R, R_1 = $-(CH_2)_3-$

SCHEME 2

^{1}H nmr spectra of *E* and *Z* **9a-c** indicate that in all cases the major isomers have the *E* configuration bearing the sulfoxyllic oxygen in a pseudo-axial and the ethoxy group on C_6 in a pseudo-equatorial arrangement. Indeed the *J* values for protons at C_6 are in the range 1.4-2.0 and 7.6-10.2 Hz respectively indicating for the latter an axial position. Moreover the deshielding effect of the sulfoxide group is enhanced for the equatorial proton at C_5 thus indicating a proximity of the sulfoxyllic oxygen laying in axial position.

Similar arguments hold for the minor isomers which have a *Z* configuration with both the sulfoxyllic oxygen and the ethoxy group laying in axial position (see experimental). Similarly the *J* values of derivatives **10a** and **10b** indicate that the sulfoxyllic oxygen lay in axial position.



9a (60%) *E/Z*=57/43 **9b** (94%) *E/Z*=58/42 **9c** (95%) *E/Z*=60/40 **10a** (58%) **10b** (88%)

Figure 1: Yields and *E/Z* ratios of sulfoxides **9** and **10**

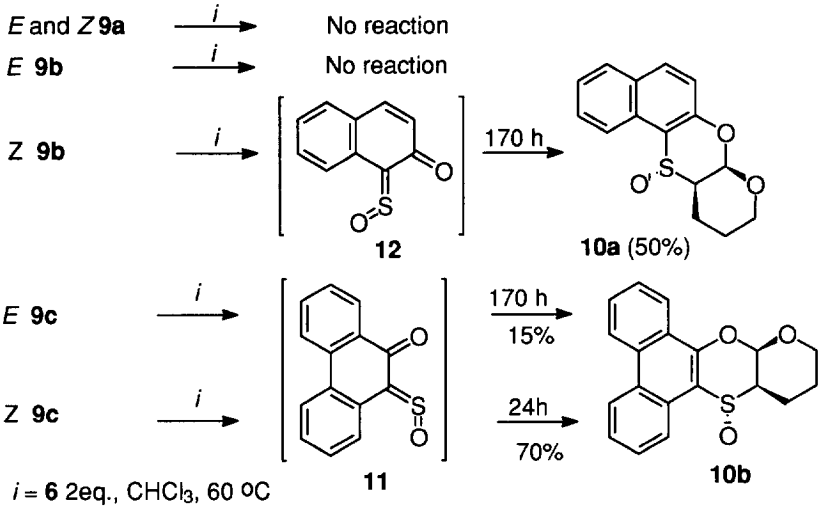
The assignment of the stereochemistry of **10b** was confirmed by X-ray crystallographic analysis which shows that the oxygen on sulfur is in a pseudo-axial position and the pyran ring has a chair conformation with the C_5-sulfur bond equatorial and the C_6-oxathiin-oxygen axial in agreement with our previous results on the structure of similar oxathiin systems.[1,4,6]

We verified whether a thermal Retro Diels-Alder (RDA) process could occur from benzo-oxathiin-*S*-oxides as it happens for the corresponding aliphatic species.[1] Having in our hands derivatives *E* and *Z* **9a-c** we could check both the role of the nature of aromatic system involved, since the transformation of oxathiins into sulfine implies loss of aromaticity, and the effect of the geometry of the starting sulfoxide in the generation of the *ortho*-thioquinone-*S*-oxides.

When sulfoxides *E* **9a-c** were heated for 7 days at 60 °C in chloroform in the presence of 2 equivalents of dihydropyrane **6**, *E*-**9a** and *E*-**9b** were found to be unreactive, but for *E*-**9c** we detected the formation of cycloadduct **10b** (less than 15% by ^{1}H nmr) indicating that the *ortho*-thioquinone-*S*-oxide **11** can be generated from *E*-**9c** and trapped as electron poor diene albeit at a quite slow rate.

A different result was observed for derivatives *Z* **9a-c**. Compound *Z*-**9a** was still unchanged even after 7 days at 60 °C, while after the same time only 30% of *Z*-**9b** remained in the crude mixture from which cycloadduct **10a** was isolated in 50% yield, indicating the formation of the acyl sulfine **12**.

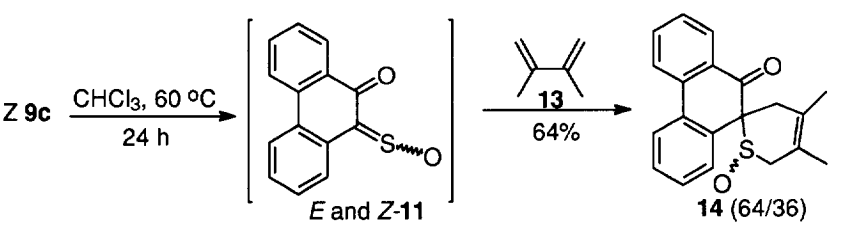
Sulfoxide *Z*-**9c** was completely consumed after 24 hours at 60 °C and cycloadduct **10b** was isolated in 70% yield (SCHEME 3).



SCHEME 3

Thus *ortho*-thioquinone-*S*-oxides **11** and **12** can be generated following this procedure and trapped as electron poor dienes. Both the aromatic system involved and the sulfoxide geometry are crucial factors for the achievement of the RDA process.

The formation of *ortho*-thioquinone-*S*-oxide **11** is also supported by its trapping as dienophile using an electron rich diene in typical Diels-Alder reactions of sulfines.[7]



SCHEME 4

When sulfoxide *Z* **9c** was heated for 24 h at 60°C in chloroform in the presence of two equivalents of 2,3-dimethyl-1,3-butadiene **13,** the spiro derivative **14** was isolated in 64% yield. As already reported,[1] RDA

processes of oxathiin-*S*-oxides afford mixtures of *E* and *Z* α-oxosulfines. Indeed thiopyrane **14** was obtained as a 64:36 mixture of diastereoisomers and consequently sulfoxide *Z* **9c**, despite used as single stereoisomer, afforded both *E* and *Z* sulfine **11** (SCHEME 4). It should be pointed out that the formation of the spiro dihydrothiopyrane **14** proves that the sulfine **11** is the real intermediate generated by thermal RDA from sulfoxide **9c**, since only the formation of a carbon sulfur double bond allows the cycloaddition to a 1,3-diene.

Attempts to isolate the sulfine **11** led to the formation of 9,10-phenthraquinone which was identified by comparison with an authentic sample. Sulfur extrusion with formation of the carbonyl species, has often been indicated as one of the decomposition patterns of sulfine.[7]

CONCLUSIONS

In conclusion we have shown that benzo-oxathiin-*S*-oxides represent an access to particular *ortho*-thiquinone-*S*-oxides which can be obtained in mild conditions as function of the aromatic system involved in the RDA reaction and of the geometry of the starting sulfoxides. The reactivity of *ortho*-thioquinone-*S*-oxides parallels that of aliphatic α-acyl sulfines in that they can act both as dienophiles and as dienes. With the aid of ^{1}H nmr and X-ray analysis we could attribute the correct geometry to the oxathiin-*S*-oxides systems which in any case shows a half boat conformation with the sulfoxyllic oxygen in a pseudo-axial position.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded (when not specified) in $CDCl_3$ at 200 and 50 MHz respectively, using residual $CHCl_3$ at 7.26 ppm for ^{1}H and central peak of $CDCl_3$ at 77 ppm for ^{13}C as reference lines. Mass spectra and GC-MS analysis were obtained using a gaschromatograph, equipped with a OV101 30 m. capillary column, interfaced on a mass spectrometer. Measurements of diffraction were carried out on a Philips PW 1100 diffractometer. Melting points are uncorrected. $CHCl_3$ and CH_2Cl_2, were dried following standard procedures, all commercial reagents were used without further purification as obtained from freshly opened containers. Synthesis of phthalimidesulfenyl chloride **1**[6] and arylthiophthalimides **3a-c**[2] have been reported elsewhere.

General procedure for the preparation of benzo-oxathiin heterocycles **7a-c** *and* **8a,b**.

Benzo-oxathiins **7a-c** and **8a,b** have been prepared by heating in chloroform at 60 °C derivatives **3a-c** in the presence of 1 equivalent of pyridine and 2 equivalents of the required enol ether.[3,4] Physical and spectroscopic data are as follows.

1,4-benzo-oxathiin **7a.** Yellow oil (ethyl acetate/petroleum ether = 1/6), 83%. ^{1}H NMR δ 1.23 (t, 3H, J = 7.0 Hz); 3.06 (2H, AB part of an ABX system, J_{AB} = 12.8 Hz); 3.62÷3.78 (m, 1H); 3.84÷4.00 (m, 1H); 3.72 (s, 3H); 5.31 (1H, X part of an ABX system, J = 4.4 and 2.2 Hz); 6.55÷6.62 (m, 2H Arom.); 6.75÷6.80 (m, 1H Arom.). ^{13}C NMR δ 15.0 (q); 29.2 (t); 55.6 (q); 64.1 (t); 93.9 (d); 111.0, 112.4 and 119.4 (d); 118.3 (s); 143.2 (s); 154.0 (s). MS *m/z* (rel. int.) 226 (100); 165 (41); 126 (51). Anal. Calcd. for $C_{11}H_{14}O_3S$. C, 58.38; H, 6.24. Found: C, 58.23; H, 6.33.

1,4-benzo-oxathiin **7b.** Glassy solid (ethyl acetate/petroleum ether = 1/6), 81%. ^{1}H NMR δ 1.26 (t, 3H, J = 7.0 Hz); 3.19 (2H, AB part of an ABX system, J_{AB} = 13.0); 4.10÷3.70 (m, 2H); 5.49 (1H, X part of an ABX system, J = 4.4 and 2.6 Hz); 7.07 (d, 1H Arom., J = 8.8 Hz); 7.56÷7.32 (m, 3H Arom.); 7.75 (d, 1H Arom., J = 8.2 Hz); 7.9 (d, 1H Arom, J = 8.8 Hz). ^{13}C NMR δ 15.6 (q); 29.3 (t); 64.9 (t); 94.8 (d); 111.4 (s); 120.3, 128.7, 126.8, 126.5, 124.7 and 123,1 (d); 129.9, 131.5 and 147.7 (s). MS *m/z* (rel. int.) 246 (79); 201 (13); 185 (100). Anal. Calcd. for $C_{14}H_{14}O_2S$. C, 68.27; H, 5.73. Found: C, 68.32; H, 5.68.

1,4-benzo-oxathiin **7c.** White solid, m.p. 105-107 °C (ethyl acetate/petroleum ether = 1/6), 89%. ^{1}H NMR δ 1.29 (t, 3H, J = 7.2 Hz); 3.30 (2H, AB part of an ABX system, J_{AB} = 12.8 Hz); 3.78÷3.93 (m, 1H); 4.01÷4.16 (m, 1H); 5.66

(1H, X part of an ABX system, J = 2.2 and 4.4 Hz); 7.52÷7.66 (m, 4H Arom.); 7.98÷8.03 (m, 1H Arom.); 8.22÷8.29 (m, 1H Arom.); 8.60÷8.64 (m, 2H Arom.). Anal. Calcd. for $C_{18}H_{16}O_2S$. C, 72.95; H, 5.44. Found: C, 73.20; H, 5.20.

1,4-benzo-oxathiin **8a.** Oil (ethyl acetate/petroleum ether = 1/8), 84%. ^{1}H NMR δ 1.66÷2.03 (m, 4H); 3.28÷3.40 (m, 1H); 3.70÷3.88 (m, 1H); 4.00÷4.17 (m, 1H); 5.68 (d, 1H, J = 2.6 Hz); 7.16 (d, 1H Arom, J = 9.0 Hz); 7.34÷7.60 (m, 3H Arom.); 7.76 (d, 1H Arom., J = 8.4 Hz); 7.89 (d, 1H Arom., J = 9.0 Hz). ^{13}C NMR δ 25.0 (t); 25.9 (t); 36.4 (d); 61.0 (t); 93.9 (d); 107.8 (s); 119.2, 122.8, 124.1, 126.2, 126.3 and 128.2 (d); 129.5 (s); 131.0 (s); 148.2 (s). MS *m/z* (rel. int.) 258 (100); 225 (14); 84 (65). Anal. Calcd. for $C_{15}H_{14}O_2S$. C, 69.74; H, 5.46. Found: C, 69.56; H, 5.67.

1,4-benzo-oxathiin **8b.** White solid, m.p. 135-137 °C (ethyl acetate/petroleum ether = 1/6), 92%. ^{1}H NMR δ 1.71÷2.03 (m, 4H); 3.39÷3.48 (m, 1H); 3.80÷3.89 (m, 1H); 4.14÷4.26 (m, 1H); 5.85 (d, 1H, J = 2.6 Hz); 7.51÷7.66 (m, 4H Arom.); 7.93÷7.98 (m, 1H Arom.); 8.34÷8.42 (m, 1H Arom.); 8.56÷8.64 (m, 2H Arom.). Anal. Calcd. for $C_{19}H_{16}O_2S$. C, 74.00; H, 5.23. Found: C, 69.86; H, 5.46.

General procedure for the synthesis of benzo-oxathiin-S-oxides **9a-c** *and* **10a,b**.

The oxidation of derivatives **7a-c** and **8a,b** have been performed using 1 equivalent of *meta*-chloroperoxybenzoic as descrided for the synthesis of oxathiin-*S*-oxides.[1] Physical and spectroscopic data of sulfoxides **9a-c** and **10a,b** are as follow:

1,4-benzo-oxathiin-S-Oxides **9a.** Glassy solid 60% (ethyl acetate/petroleum ether = 2.5/1), (*E*/*Z* = 57/43):

E isomer, glassy solid. ^{1}H NMR δ 1.28 (t, 3H, J = 7.1 Hz); 3.22 (2H, AB part of an ABX system, J_{AB} = 13.4 Hz); 3.66÷3.79 (m, 1H); 3.81 (s, 3H); 3.97÷4.13 (m, 1H); 5.55 (1H, X part of an ABX system, J = 2.0 and 7.6 Hz); 6.93÷7.14 (m, 3H Arom.) . MS *m/z* (rel. int.) 242 (79); 194 (37); 170 (100). Anal. Calcd. for $C_{11}H_{14}O_4S$. C, 54.53; H, 5.82. Found: C, 54.67; H, 5.76. *Z* isomer, oil. ^{1}H NMR δ 1.22 (t, 3H, J = 6.9 Hz); 3.41 (2H, AB part of an ABX system, J_{AB} = 13.6 Hz); 3.60÷3.75 (m, 1H); 3.83 (s, 3H); 3.85÷3.95 (m, 1H); 5.49 (1H, X part of an ABX system, J = 3.6 and 5.0 Hz); 6.92÷7.24 (m, 3H Arom.).

1,4-benzo-oxathiin-S-Oxides **9b**. 94% (ethyl acetate/petroleum ether = 1/4), (*E*/*Z* = 58/42).

E isomer, white solid m.p. 122-124 °C. IR cm^{-1} 3050; 2979; 2931; 1619; 1596; 1563; 1039 (S=O stret.). ^{1}H NMR δ 1.36 (t, 3H, J = 7.2 Hz); 2.96 (dd, 1H, A part of an AMX system, J = 10.0 and 14.0 Hz); 3.46 (dd, 1H, M part of an AMX system, J = 1.4 and 14.0 Hz); 3.78÷3.93 (m, 1H); 4.13÷4.29 (m, 1H); 5.75 (dd, 1H, X part of an AMX system, J = 1.4 and 10.0 Hz); 7.16 (d, 1H Arom., J = 8.8 Hz); 7.41÷7.68 (m, 2H Arom.); 7.80 (d, 1H Arom., J = 8.2 Hz); 7.91 (d, 1H Arom., J = 9.2 Hz); 8.46 (d, 1H Arom., J = 8.8 Hz). ^{13}C NMR δ 15.1 (q); 47.2 (t); 66.3 (t); 93.1 (d); 115.2 (s); 119.5, 121.9, 125.1, 128.5, 128.6 and 129.0 (d); 132.2, 135.0 and 151.3 (s). MS *m/z* (rel. int.) 262 (15); 190 (37); 114 (100). Anal. Calcd. for $C_{14}H_{14}O_3S$. C, 64.10; H, 5.38. Found: C, 63.97; H, 5.35.

Z isomer, white solid m.p. 96-98 °C. IR cm^{-1} 3050; 2978; 1618; 1597; 1564; 1049 (S=O stret.). ^{1}H NMR δ 1.23 (t, 3H, J = 7.0 Hz); 3.23 (dd, 1H, A part of an AMX system, J = 2.6 and 14.8 Hz); 3.68÷3.98 (m, 3H); 5.72 (bt, 1H, X part of an AMX system, J = 2.6 Hz); 7.17 (d, 1H Arom., J = 8.6 Hz); 7.43÷7.68 (m, 2H Arom.); 7.82 (d, 1H Arom., J = 8.0 Hz); 7.92 (d, 1H Arom., J = 9.0 Hz); 8.56 (d, 1H Arom., J = 8.6 Hz). ^{13}C NMR δ 14.8 (q); 47.8 (t); 65.4 (t); 92.7 (d); 116.0 (s); 119.7, 122.6, 125.1, 128.3, 128.5 and 129.6 (d); 132.6, 134.5, 147.2 (s). MS *m/z* (rel. int.) 262 (7); 190 (38); 134 (100).

1,4-benzo-oxathiin-S-Oxides **9c**: 95% (ethyl acetate/petroleum ether = 1/1), (*E*/*Z* = 60/40):

E isomer, white solid m.p. 168 °C dec. ^{1}H NMR δ 1.46 (t, 3H, J = 7.0 Hz); 3.05 (dd, 1H, A part of an AMX system, J = 10.2 and 14.2 Hz); 3.55 (dd, 1H, , M part of an AMX system, J = 1.4 and 14.2 Hz); 3.90÷4.06 (m, 1H); 4.29÷4.45 (m, 1H); 5.92 (dd, 1H, X part of an AMX system, J = 1.4 and 10.2 Hz); 7.56÷7.83 (m, 4H Arom.); 8.41÷8.66 (m, 4H Arom.). ^{13}C NMR δ 15.3 (q); 47.5 (t); 66.6 (t); 94.0 (d); 112.7 (s); 122.7, 122.8, 123.0 and 124.0 (d); 125.2 (s); 125.8 (d); 126.5 (s); 127.20 and 128.20 (d); 129.7 (s); 129.8 (d); 133.1 and 148.1 (s). MS *m/z* (rel. int.) 312 (15); 264 (18); 240 (100). Anal. Calcd. for $C_{18}H_{16}O_3S$. C, 69.21; H, 5.16. Found: C, 69.10; H, 4.85.

Z isomer, white solid m.p. 128 °C dec. ^{1}H NMR δ 1.24 (t, 3H, J = 7.1 Hz); 3.36 (dd, 1H, A part of an AMX system, J = 2.7 and 14.8 Hz); 3.74÷4.02 (m, 3H); 5.95 (bt, 1H, X part of an AMX system, J = 2.7 Hz); 7.57÷7.83 (m, 4H Arom); 8.46 (dd, 1H Arom., J = 1.4 and 7.9 Hz); 8.62÷8.69 (m, 3H Arom.). ^{13}C NMR δ 15.7 (q); 47.9 (t); 65.8 (t); 93.0 (d); 113.5 (s); 122.8, 122.9, 123.5, 123.8 (d); 125.4 (s); 125.8 (d); 126.9 (s); 127.21 and 128.07 (d) 129.4 (s); 130.0 (d); 133.0 and 143.95 (s). MS *m/z* (rel. int.) 312 (4); 264 (5); 240 (100).

1,4-benzo-oxathiin-S-Oxide **10a**: White solid, m.p. 104-108 °C (ethyl acetate/petroleum ether = 2/1), 58%. IR cm^{-1} 3070; 2947; 1618; 1596; 1564; 1232; 1035 (S=O stret.). ^1H NMR δ 1.14÷1.40 (m, 1H); 1.66÷2.00 (m, 3H); 3.36÷3.48 (m, 1H); 3.83÷3.94 (m, 1H); 4.03÷4.20 (m, 1H); 6.01 (d, 1H, J = 2.2 Hz); 7.21 (d, 1H Arom, J = 9.0 Hz); 7.40÷7.68 (m, 2H Arom.); 7.80 (d, 1H Arom., J = 8.4 Hz); 7.91 (d, 1H Arom., J = 9.0 Hz); 8.44 (d, 1H Arom., J = 8.4 Hz). ^{13}C NMR δ 17.7 (t); 24.3 (t); 52.4 (d); 61.0 (t); 89.2 (d); 112.6 (s); 119.3, 121.7, 125.0, 128.5 and 128.6 (d); 129.1 and 132.3 (s); 135.0 (d); 151.3 (s). MS *m/z* (rel. int.) 274 (8); 190 (4); 84 (72); 83 (100). Anal. Calcd. for $C_{15}H_{14}O_3S$. C, 65.67; H, 5.14. Found: C, 66.00; H, 5.04.

1,4-benzo-oxathiin-S-Oxide **10b**: White solid, m.p. 160 °C dec. (ethyl acetate/petroleum ether = 1/1), 88%. IR cm^{-1} 3080; 2939; 1608; 1582; 1524; 1041 (S=O stret.). ^1H NMR δ .28÷1.41 (m, 1H); 1.70÷1.81 (m, 1H); 1.89÷2.13 (m, 2H); 3.46÷3.55 (m, 1H); 3.96÷4.33 (m, 2H); 6.19 (d, 1H, J = 2.2 Hz); 7.57÷7.85 (m, 4H Arom.); 8.51÷8.67 (m, 4H Arom.). ^{13}C NMR δ 17.9 (t); 24.3 (t); 52.7 (d); 61.46 (t); 89.9 (d); 110.1 (s); 122.7, 122.8, 123.0, 124.1, 124.9, 125.8, 126.7, 127.3, 128.2, 129.80, 129.84, 133.15 and 148.0 (8 doublets and 5 singlets). MS *m/z* (rel. int.) 324 (4); 276 (5); 240 (100). Anal. Calcd. for $C_{19}H_{16}O_3S$. C, 70.35; H, 4.97: Found: C, 69.95; H, 4.72. X-ray data: lists of refined coordinates, e.s.d's and final atomic parameters are given as supplementary material.

Synthesis of Dihydrothiopyran-S-Oxides **14**. Derivative **Z-9c** 31.2 mg (1 mmol) was heated in chloroform at 60 °C for 24 hours in the presence of 2,3-dimethyl-1,3-diene 16.4 mg (2 mmol). Evaporation of the solvent and flash chromatography (ethyl acetate/petroleum ether = 1/3), afforded spiro derivative 14 (64% yield) as a 64/46 mixture of unseparable diastereoisomers, an asterisk indicates signals of major isomer. ^1H NMR δ 1.79 (bs, 6H)*; 1.87 (bs, 3H)*; 2.02 (bs, 3H); 2.40÷2.56 (m, 1H); 2.74÷3.30 (m, 3H)*; 3.38÷3.56 (m, 1H)*; 3.82÷3.98 (m, 1H); 7.30÷7.75 and 7.90÷8.10 (m, 8H arom)*. Anal. Calcd. for $C_{20}H_{18}O_2S$. C, 74.50; H, 5.63: Found: C, 74.60; H, 5.82.

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