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Graphical Abstract

Stereoisomerization of α-hydroxy-β-sulfenyl-α,β-dimethyl naphthoquinones controlled by nonbonded sulfur–oxygen interactions **pp 1–4**

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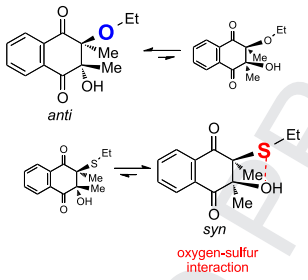

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Stereoisomerization of α-hydroxy-β-sulfenyl-α,β-dimethyl naphthoquinones controlled by nonbonded sulfur–oxygen interactions

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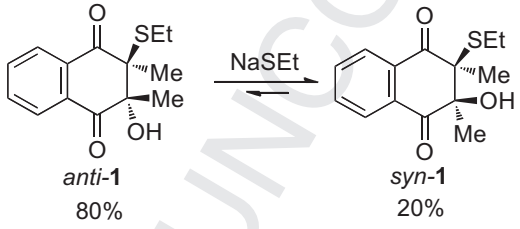
ABSTRACT

The anti α-hydroxy-β-sulfenyl-α,β-dimethyl naphthoquinones isomerize in basic media into syn/anti mixtures of isomers, giving the syn isomer as the major product. Conversely, *anti* α-hydroxy-β-alkoxy-α,β-dimethyl naphthoquinones isomerize to furnish the anti isomer as the major product. The crystal structure of *syn* α-hydroxy-β-phenylsulfenyl-α,β-dimethyl naphthoquinone has been determined. The X-ray and experimental work demonstrated that an attractive 1,4 intramolecular interaction of divalent sulfur with hydroxyl oxygen is the driving force for the aforementioned stereochemical preference.

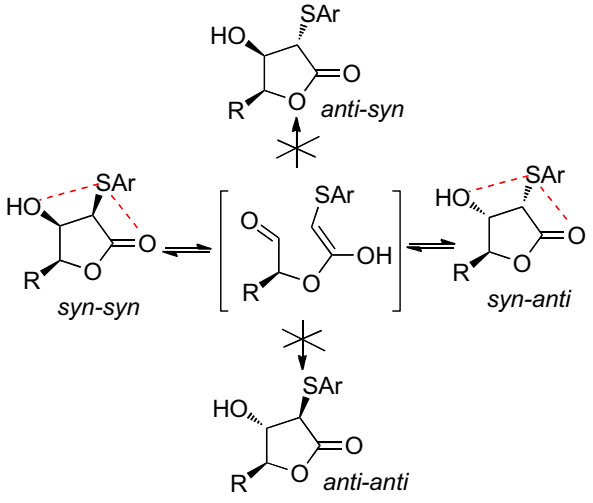
1. Introduction

In 1981, Silverman investigated the mechanism of vitamin K epoxide-reductase using 2,3-dimethyl-1,4-naphthoquinone 2,3-epoxide as a model for vitamin K 2,3-epoxide.[1,2] This study advanced our understanding of the mechanism of vitamin K epoxide-reductase during the catalytic conversion of vitamin K 2,3-epoxide into vitamin K, which is essential for blood coagulation. This author reported that *anti* α-hydroxy-β-ethylsulfenyl-α,β-dimethyl naphthoquinone (*anti*-**1**) isomerized into an 8:2 mixture of syn/anti isomers when treated with sodium ethylthiolate (Scheme 1) through a retro-aldol/aldol mechanism. A similar result was observed for α-hydroxy-β-phenylsulfenyl-α,β-dimethyl naphthoquinone **2**.[2]



Scheme 1. Isomerization of naphthoquinone derivatives.

We have recently reported that *syn–anti*-β-hydroxy-α-sulfenyl-γ-butyrolactones isomerized into *syn–syn*-β-hydroxy-α-sulfenyl-γ-butyrolactones (Scheme 2).[3] We proposed that nonbonded sulfur–oxygen interactions could control the stereoselectivity of the reaction. When we determined the crystal structures of *syn–syn* lactones, we observed that the sulfur–oxygen distances were less than the sum of the Van der Waals radii (3.3 Å), with the angle formed by the hydroxyl oxygen, sulfur, and quaternary aromatic carbon being approximately 180°. In addition, the carbonylic oxygen–sulfur was directed <40° from the perpendicular to the C–S–C. Then two concomitant, attractive 1,4 intramolecular interactions of divalent sulfur with both the carbonyl and the hydroxyl oxygens served as the driving force to establish the stereochemical preference.



Scheme 2. Isomerization of β-hydroxy-α-sulfenyl-γ-butyrolactones.

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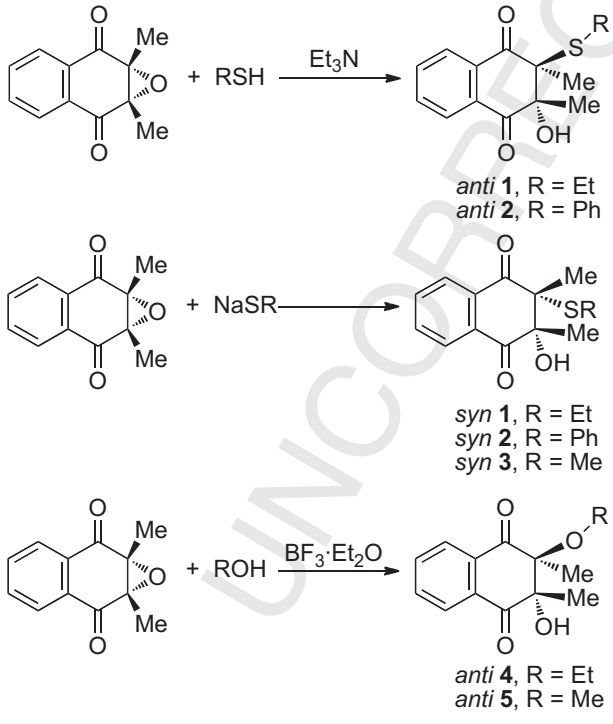
Weak nonbonding interactions between sulfur and oxygen atoms have been invoked to explain the biological activities as well as their physical properties in a large number of organosulfur compounds.[4]

2. Results and discussion

Herein, we show that for α-hydroxy-β-sulfenyl-α,β-dimethyl naphthoquinones, the intramolecular interaction of divalent sulfur with the hydroxyl oxygen also control the stereochemical preference. The crystal structure of *syn* α-hydroxy-β-sulfenyl-α,β-dimethyl naphthoquinone has been determined. Also α-hydroxy-β-alkoxy-α,β-dimethyl naphthoquinones have been prepared for comparison. The isomerization of these oxygenated analogs under the same conditions as the sulfurated ones gave either the anti isomer or an equal mixture of syn/anti isomers.

α-Hydroxy-β-sulfenyl-α,β-dimethyl naphthoquinones *anti*-**1** and *anti*-**2** were prepared starting from the epoxide[5] using the corresponding thiol in the presence of triethylamine.[2] Having already reported compounds **1** and **2**, we went on to prepare compound *syn* **3** resulting from the opening of the epoxide with sodium methyl thiolate and further isomerization.[6] This reaction furnished a mixture of isomers with the syn isomer predominating.

For the preparation of the oxygenated derivatives, acidic conditions were required. The epoxide was opened with the corresponding alcohol[7] using boron trifluoride as a catalyst using conditions we had previously reported.[8] These reactions resulted to be very slow (see Experimental section). During the coagulation cascade,[9] accordingly vitamin-K-epoxide is selectively opened by a cysteine residue of vitamin-K-epoxide reductase, but it is not opened by the coagulation factors, which are serine proteases (Scheme 3).



Scheme 3. Preparation of substrates.

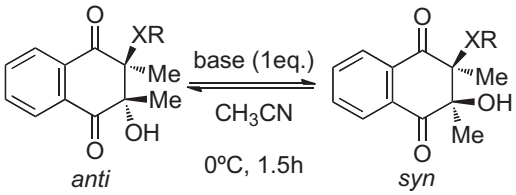
Compounds **1**–**5** were submitted to the isomerization reaction using sodium ethylthiolate or sodium phenylthiolate. Compounds **1** and **2** gave the same results as previously reported, giving rise to the syn isomer as the major form.[2] Similar results were also obtained for methyl sulfenyl derivative **3**. syn-isomers **1**–**3** (or anti isomers **1**–**3** or any mixture of both) invariably isomerized into a mixture of syn/anti lactones, with the syn isomer being the major one in all cases (entries 1–9, Table 1). As already reported,[2,10] the elimination product was also obtained in some cases (Table 1). In contrast to β-hydroxy-α-sulfenyl-γ-butyrolactones,[3] compounds **1**–**3** did not isomerize in the presence of bases, such as triethylamine or *N*-methylmorpholine.

Table 1
Ratio of syn/anti isomers resulting from isomerization

Entry	Substrate	Base	anti/syn
1	*syn* **1**	NaSEt	14/65[a]
2	*anti* **1**	NaSEt	14/71[a]
3	*syn* **1**	NaSPh	5/83[a]
4	*syn* **2**	NaSEt	17/83
5	*syn* **2**	NaSPh	13/61[a]
6	*anti* **2**	NaSEt	27/68[a]
7	*anti* **2**	NaSPh	28/69[a]
8	*syn* **3**	NaSEt	8/82[a]
9	*syn* **3**	NaSPh	20/80
10	*anti* **4**	NaSEt	70/30
11	*anti* **4**	NaSPh	>95/5
12	*anti* **5**	NaSEt	58/42
13	*anti* **5**	NaSPh	38/62

[a] Elimination product was already obtained.

When oxygenated substrates **4**–**5** were submitted to the same reaction conditions as their sulfurated counterparts, they underwent an isomerization that furnished a mixture of isomers (entries 10–13, Table 1). Compound **4** was treated with sodium ethylthiolate and sodium phenylthiolate giving rise to a mixture of isomers, with the main product being the anti isomer (entries 10 and 11). This result is opposite to the one observed starting from sulfurated compound **1**, which furnished the syn isomer under the same conditions (compare 1–3 with 10–11 entries). Similarly compound **5** gave an equal mixture of syn/anti isomers whilst **3** gave the syn isomer as the main product (compare 8–9 with 12–13 entries). No elimination products were observed for compounds **4**–**5**, as expected. Silverman had previously suggested an elimination mechanism through the formation of disulfide for compound **4**.[2]



The crystal structure of compound *syn* **2** has been determined (Fig. 1).[11] The distance between the hydroxyl oxygen and sulfur was 2.97 Å. The azimuthal angle was φ=113.7° and polar angle was θ=99.4° for the sulfur–hydroxyl oxygen contact. These geometric features are similar to the ones depicted for β-hydroxy-α-sulfenyl-γ-butyrolactones.[3] For them, the azimuthal angles and polar angles for sulfur–hydroxyl oxygen contacts were 107° and 93°, respectively.

The short atomic distance observed is interpreted as a nonbonded interaction between oxygen and sulfur atoms, an interaction that would stabilize the syn isomer.

The linear alignment of the C–S covalent bond and the coordinating hydroxyl oxygen should allows an effective orbital interaction between the oxygen lone electron pair and the σ* orbital

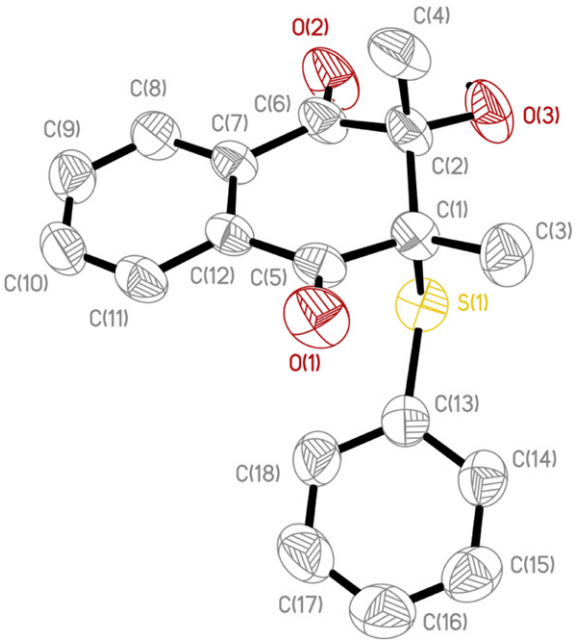


Fig. 1. X-ray structure of compound *syn*-**2**.

of the S–C bond, which may elongate the S–C bond (1.77 Å for *syn* **2**, 1.75 Å for the diphenyl disulfide). The phenyl ring attached to the sulfur atom is oriented away from the hydroxyl, permitting the interaction to take place. Sulfur–oxygen interactions type I have nucleophilic oxygen tending to approach along the extension of the covalent bonds to sulfur.[12]

The distance between the carbonyl oxygen and sulfur was 3.55 Å. For this contact, the azimuthal angle was 94.9° and the polar angle was 97.9°. These parameters cannot be attributed to a sulfur–oxygen interaction. The planar structure of the naphthoquinone imposes rigidity that does not permit the sulfur atom to contact the carbonyl oxygen. This orientation might be at the origin of the lower selectivity observed during isomerization of compounds **1**–**3** as compared to the β-hydroxy-α-sulfenyl-γ-butyrolactones.

3. Conclusions

In summary, an attractive 1,4 intramolecular interaction of divalent sulfur with hydroxyl oxygen has been observed in the X-ray structure of *syn* α-hydroxy-β-phenylsulfenyl-α,β-dimethyl naphthoquinone. This sulfur–oxygen interaction can be invoked to account for the tendency of α-hydroxy-β-sulfenyl-α,β-dimethyl naphthoquinones to assume the syn configuration. This study should contribute to the understanding of the role played by this subtle noncovalent interaction in determining the biochemical processing of vitamin-K-epoxide during blood coagulation.

4. Experimental section

4.1. General experimental methods

All solvents used in reactions were freshly distilled from appropriate drying agents before use. ^{1}H NMR spectra and ^{13}C NMR spectra were measured in $CDCl_3$ (^{1}H, 7.24 ppm; ^{13}C 77.0 ppm) solution at 30 °C on a 300 MHz or a 500 MHz NMR spectrometer. Mass spectra were measured in a hybrid quadrupole-t-TOF mass spectrometer operating at a resolution ca. 15000 FWHM (W-mode) with an orthogonal Z-spray-electrospray interface was used. The drying gas as well as nebulizing gas was nitrogen at a flow of 400 and 60 L/h, respectively. The temperature of the source block was set to 120 °C and the desolvation temperature to 150 °C. A capillary voltage of 3 kV was used in the positive scan mode, and the cone voltage was set to 15 V. Sample solutions were infused via syringe pump directly connected to the ESI source at a flow rate of 10 μL/min. ESI mass spectra were dominated by the presence of sodium adducts of the target compound. For the accurate mass measurements, a 2 mg/L standard solution of leucine enkephalin was introduced via the lock spray needle at a cone voltage set to 45 V and a flow rate of 30 μL/min. IR spectra were recorded as oil films or KBr discs or NaCl pellets on a FT-IR spectrometer. EM Science Silica Gel 60 was used for column chromatography while TLC was performed with precoated plates (Kieselgel 60, F_{254}, 0.25 mm). Unless otherwise specified, all reactions were carried out under nitrogen atmosphere with magnetic stirring.

4.2. General experimental procedure for the preparation of thioethers *anti*-1 and *anti*-2

To an ice-bath cold solution of 2,3-dimethyl-1,4-naphthoquinone-2,3-epoxide (202 mg, 1.0 mmol) in dry acetonitrile (2.0 mL) was added drop wise the corresponding thiol (3.0 mmol) and then triethylamine (140 μL, 1.0 mmol). The resulting mixture was stirred cold with an ice-bath for 3.5 h. Then was quenched with dichloromethane (15 mL) and 5% Na_2CO_3 (15 mL). The organic layer was separated, the aqueous layer was extracted with dichloromethane (3×15 mL), and then the organic layers were dried (Na_2SO_4) and concentrated. The crude was purified through chromatography (silica-gel, hexanes/ethyl acetate (7:3)) to afford the desired compound. The resulting solid mixture was recrystallized from hexanes.

*4.2.1. (2R,3S)-2-(Ethylthio)-3-hydroxy-2,3-dimethyl-2,3-dihydronaphthalene-1,4-dione anti-**1**.* Recrystallized from hexanes gave white crystals, mp 91–92 °C (lit.[2] 93–93.5 °C) (Yield=251 mg, 95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (1H, d, *J*=7.3 Hz), 7.85 (1H, d, *J*=7.2 Hz), 7.57–7.64 (2H, m), 3.84 (1H, br s), 2.44 (m, 1H), 2.16 (m, 1H), 1.64 (3H, s), 1.55 (3H, s), 1.00 (3H, t, *J*=7.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.2, 192.8, 134.1, 133.8, 132.7, 132.2, 127.1, 126.8, 80.2, 60.9, 23.8, 18.5, 16.3, 13.8 ppm. IR (NaCl) δ 3018, 2951, 2930, 1696, 1595, 1539, 1455, 1371, 1281, 1188, 1110, 1016, 975, 937 cm^{-1}. HRMS *m*/*z* calcd for $C_{14}H_{16}O_3SNa$ [M+Na$^+$]: 287.0718, found: 287.0720.

*4.2.2. (2R,3S)-2-Hydroxy-2,3-dimethyl-3-(phenylthio)-2,3-dihydronaphthalene-1,4-dione anti-**2**.* Recrystallized from hexanes gave white crystals, mp 109–112 °C (lit.[2] 115.5–116.5 °C) (Yield=287 mg, 92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87–7.98 (2H, m), 7.62–7.67 (2H, m), 7.13–7.32 (2H, m), 3.64 (1H, s), 1.68 (3H, s), 1.58 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.9, 192.7, 137.0, 134.2, 133.8, 133.5, 132.2, 129.9, 128.8, 127.2, 127.0, 80.2, 64.4, 18.5, 17.0 ppm. IR (NaCl) δ 3035, 2929, 1698, 1601, 1507, 1370, 1113, 1047, 949, 888 cm^{-1}. HRMS *m*/*z* calcd for $C_{18}H_{16}O_3SNa$ [M+Na$^+$]: 335.0718, found: 335.0719.

4.3. General experimental procedure for the preparation of thioethers *syn*-1, *syn*-2 and *syn*-3

To an ice-bath cold solution of 2,3-dimethyl-1,4-naphthoquinone-2,3-epoxide (202 mg, 1.0 mmol) in dry tetrahydrofuran (5.0 mL) was added drop in one portion the corresponding sodium thiolate (1.0 mmol). The resulting mixture was stirred cold with an ice-bath for 1 h. Then was quenched with dichloromethane (15 mL) and water (15 mL). The organic layer was separated, the aqueous layer was extracted with dichloromethane (3×15 mL), and then the organic layers were dried (Na_2SO_4) and

concentrated. The crude was purified through chromatography (silica-gel, hexanes/ethyl acetate (7:3)) to afford the desired compound.

*4.3.1. (2S,3S)-2-(Ethylthio)-3-hydroxy-2,3-dimethyl-2,3-dihydronaphthalene-1,4-dione syn-**1***. Yield=243 mg, 92%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03–8.06 (1H, m), 7.96–7.99 (1H, m), 7.64–7.74 (2H, m), 4.11 (1H, br s), 2.34 (m, 1H), 2.07 (m, 1H), 1.64 (3H, s), 1.26 (3H, s), 0.94 (3H, t, J=7.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.8, 191.5, 134.8, 134.1, 133.1, 131.1, 127.5, 126.7, 80.0, 62.5, 24.7, 23.7, 15.2, 13.7 ppm. IR (NaCl) δ 3040, 2930, 1730, 1600, 1442, 1332, 1225, 1159, 1068, 1025, 859, 777, 750, 597 cm^{-1}. HRMS m/z calcd for $C_{14}H_{16}O_3SNa$ [M+Na$^+$]: 287.0718, found: 287.0715.

*4.3.2. (2S,3S)-2-Hydroxy-2,3-dimethyl-3-(phenylthio)-2,3-dihydronaphthalene-1,4-dione syn-**2***. Recrystallized from CH_2Cl_2–hexanes gave white crystals, mp 86–87 °C (lit.[2] 85.5–89 °C) (Yield=281 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (1H, m), 7.92 (1H, m), 7.71–7.75 (2H, m), 7.27 (1H, t, J=7.4 Hz), 7.16 (2H, t, J=7.8 Hz), 7.06 (2H, d, J=7.3 Hz), 4.37 (1H, s), 1.66 (3H, s), 1.34 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.9, 191.3, 136.9, 135.0, 134.1, 134.0, 131.0, 129.9, 129.4, 128.8, 127.6, 126.9, 80.1, 66.5, 25.2, 16.0 ppm. IR (NaCl) δ 3060, 2980, 2935, 1885, 1731, 1563, 1442, 1330, 1253, 1160, 1075, 1025, 897, 859, 776, 691 cm^{-1}. HRMS m/z calcd for $C_{18}H_{16}O_3SNa$ [M+Na$^+$]: 335.0718, found: 335.0723.

*4.3.3. (2S,3S)-2-Hydroxy-2,3-dimethyl-3-(methylthio)-2,3-dihydronaphthalene-1,4-dione syn-**3***. Recrystallized from CH_2Cl_2–hexanes gave orange solid, mp 81–83 °C (Yield=223 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01–8.04 (1H, m), 7.93–7.96 (1H, m), 7.62–7.72 (2H, m), 4.15 (1H, br s), 1.70 (3H, s), 1.57 (3H, s), 1.26 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.9, 190.1, 134.9, 134.1, 132.9, 131.0, 127.4, 126.7, 80.0, 61.9, 25.0, 14.1, 12.4 ppm. IR (NaCl) δ 3019, 2987, 2937, 1680, 1592, 1507, 1455, 1386, 1311, 1292, 1263, 1174, 1005, 885, 713 cm^{-1}. HRMS m/z calcd for $C_{13}H_{14}O_3SNa$ [M+Na$^+$]: 273.0561, found: 273.0562.

4.4. General experimental procedure for the preparation of ethers 4–5

To an ice-bath cold solution of 2,3-dimethyl-1,4-naphthoquinone-2,3-epoxide (506 mg, 2.5 mmol) in dry dichloromethane (12.5 mL) and methanol (12.5 mL) was added drop wise boron trifluoride etherate (0.48 mL, 3.8 mmol). The resulting mixture was heated at 50 °C for 14 days. Then was quenched with saturated aqueous sodium bicarbonate (15 mL) and extracted with dichloromethane (3×15 mL), and then the organic layers were washed (brine), dried (Na_2SO_4) and concentrated. The crude was purified through chromatography (silica-gel, hexanes/ethyl acetate (7:3)) to afford the desired compound.

*4.4.1. (2S,3S)-2-Ethoxy-3-hydroxy-2,3-dimethyl-2,3-dihydronaphthalene-1,4-dione anti-**4***. White needles, mp 67–70 °C (Yield=372 mg, 60%) (Quantitative yield based on recovered starting material). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90–7.93 (2H, m), 7.59–7.64 (2H, m), 4.01 (1H, br s), 3.47–3.53 (1H, m), 3.22–3.28 (1H, m), 1.38 (3H, s), 1.34 (3H, s), 0.90 (3H, t, J=7.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.35, 197.14, 134.3, 134.0, 133.3, 132.5, 126.9, 126.8, 85.0, 81.0, 60.1, 19.3, 15.5, 13.9 ppm. IR (NaCl) δ 3046, 2981, 1697, 1507, 1456, 1276, 1054, 984, 707, 667 cm^{-1}. HRMS m/z calcd for $C_{14}H_{16}O_4Na$ [M+Na$^+$]: 271.0946, found: 271.0948.

*4.4.2. (2S,3S)-2-Hydroxy-3-methoxy-2,3-dimethyl-2,3-dihydronaphthalene-1,4-dione anti-**5***. White needles, mp 97–99 °C (Yield=322 mg, 55%) (Quantitative yield based on recovered starting material). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94–7.99 (2H, m), 7.63–7.69 (2H, m), 3.92 (1H, br s), 3.27 (3H, s), 1.37 (3H, s), 1.34 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.8, 196.8, 134.5, 134.1, 133.3, 132.2, 127.1, 127.0, 85.1, 81.3, 52.5, 20.2, 13.9 ppm. IR (NaCl) δ 3019, 2958, 2938, 1698, 1596, 1539, 1455, 1372, 1281, 1189, 1122, 1017, 938 cm^{-1}. HRMS m/z calcd for $C_{13}H_{14}O_4Na$ [M+Na$^+$]: 257.0790, found: 257.0792.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.01.033.

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6. This result is in accordance with the isomerization ratios commented below (Table 1, entries 8–9).
7. Ethanol and methanol gave desired opened product but phenol did not.
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9. Furie, B.; Furie, B. C. *Blood* **1990**, *75*, 1753–1762.
10. The elimination reaction results from the attack of thiolate to the sulfur atom and the products are the corresponding naphthoquinone and disulfide as already reported in Ref. 2.
11. The crystal structure has been deposited at the CCDC and allocated the deposition number CCDC 906980.
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