was obtained. 15: $^1$H NMR $\delta$ 1.67 (m, 4 H), 2.12 (m, 3 H, $CH_3$), 2.25 (m, 4 H), 2.88 (m, 2 H); $^{19}$F NMR $\delta$ -59.6; $^{13}$C NMR $\delta$ 14.3, 22.6, 22.7, 23.1, 25.0, 48.7 (C-3), 123.7 (q, $^1J$ = 271 Hz, $CF_3$), 130.6 (q, $^2J$ = 36 Hz, C-1), 135.1 (C-8), 137.7 (C-9), 144.6 (C-2); MS $m/e$ 202 ($M^+$, 71), 185 (M - 15, 38), 174 (M - 28, 23), 159 (30), 141 (12), 133 (41, M - $CF_3$), 115 (12), 105 (100), 91 (24), 79 (14), 77 (10), 69 (14); IR no C=O vibration.

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**Supplementary Material Available:** NMR data of products **1b**, **1c**, **2b**, **3a**, **5a**, **6a**, **9a**, **10a**, **11a**, **12a**, **13a**, **3b**, **4b**, **6b**, **8b**, **14**, and **15** (53 pages). Ordering information is given on any current masthead page.

# Use of Sulfoxides as Cocatalysts in the Palladium-Quinone-Catalyzed 1,4-Diacetoxylation of 1,3-Dienes. An Example of Ligand-Accelerated Catalysis

Helena Grennberg, Adolf Gogoll, and Jan-E. Bäckvall*

*Department of Organic Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden*

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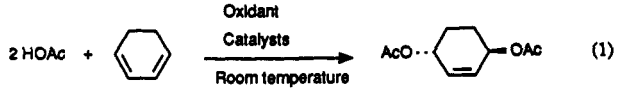
The use of sulfinyl quinones as cocatalysts in the palladium-catalyzed 1,4-diacetoxylation of 1,3-dienes improves the stereochemical outcome of the reaction by increasing the rate of the internal migration of the acetate nucleophile. A mechanism of the interaction between the sulfoxide and the intermediate ($\pi$-allyl)palladium complex, based on $^1$H NMR results, is proposed.

## Introduction

The palladium-catalyzed diacetoxylation of 1,3-dienes is a high-yielding regio- and diastereoselective reaction that gives access to synthetically useful products (eq 1).[1] To



(1)

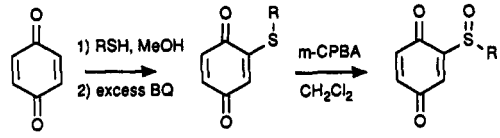
further improve the scope of this reaction, it was our objective to increase the reaction rate as well as to investigate the possibility of introducing enantioselectivity. The idea was to enhance the interaction between the intermediate ($\pi$-allyl)palladium complex and the quinone used as oxidant (or electron-transfer mediator), since this interaction is of importance for the selectivity of the reaction.[2]

Several reactions that employ 1,4-benzoquinones as stoichiometric oxidants or electron carriers in selective palladium-catalyzed oxidations have recently been developed in this group.[2-4] When the quinone is used in catalytic amounts, an external oxidant such as $MnO_2$[2] or molecular oxygen activated by a metal macrocycle[4] is employed (eq 1). In the present study molecular oxygen, activated by iron phthalocyanine (Fe(Pc)), was chosen as the external oxidant. This allows the progress of the reaction to be monitored by the oxygen consumption.

## Results and Discussion

The interaction between the ($\pi$-allyl)palladium complex and the quinone can be enhanced by increasing the electron density of the quinone itself or by introducing an additional "handle" on the quinone in the form of a coordinating substituent. Previous investigations, in which a wide variety of quinones were employed, have shown that reaction rate and selectivity are markedly dependent upon the quinone substituents.[2] This might have steric as well as electronic reasons. The best results, regarding both rate and selectivity, were obtained for the unsubstituted 1,4-benzoquinone and for quinones with an electron-withdrawing and an electron-donating group in the 2- and 3-positions, respectively. This indicates that the electron density of the quinone may not be varied much.

It is known that sulfoxides form strong complexes with Pd(II),[5] and ($\pi$-allyl)palladium(sulfoxide) species have been characterized by NMR spectroscopy.[6] Other related, weaker complexating agents are nitriles[5b,7] and DMF.[5b,8] Since the sulfoxide group has good complexation properties we decided to study 2-sulfinyl-1,4-benzoquinones **2a-c**, which are readily available from 1,4-benzoquinone (eq 2).[9]



(2)

Since these chiral sulfinyl quinones may be useful in enantioselective reactions the *R*-(+)-enantiomer of *p*-

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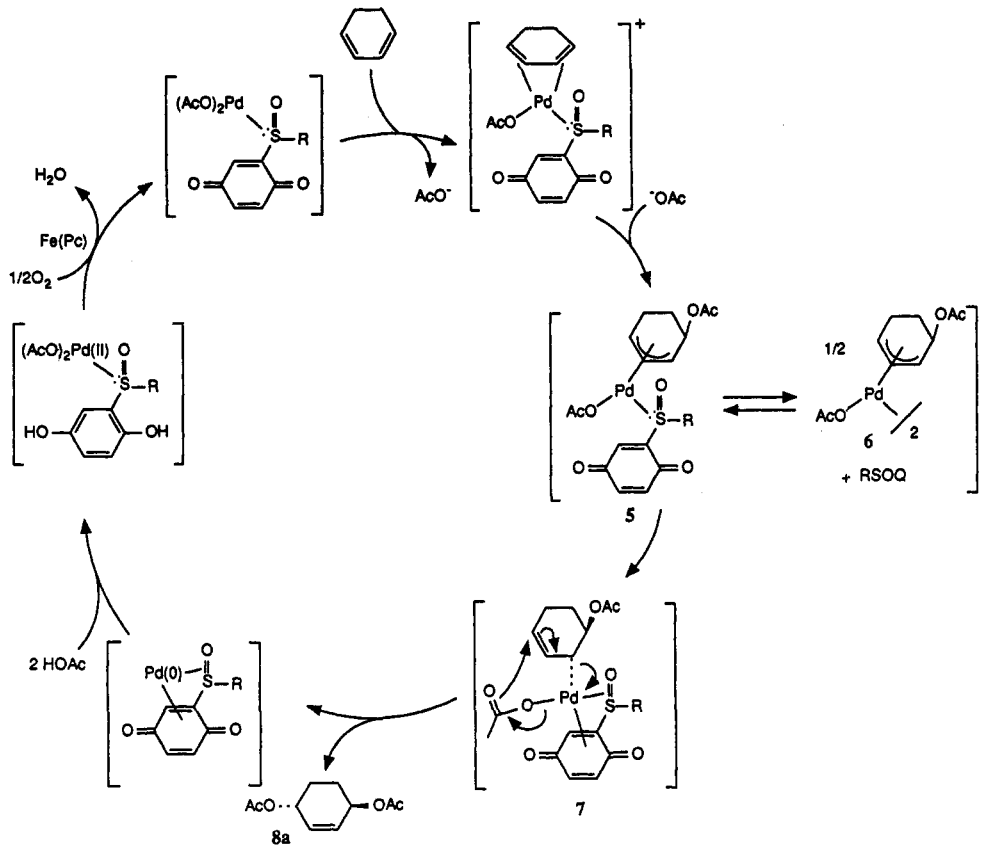
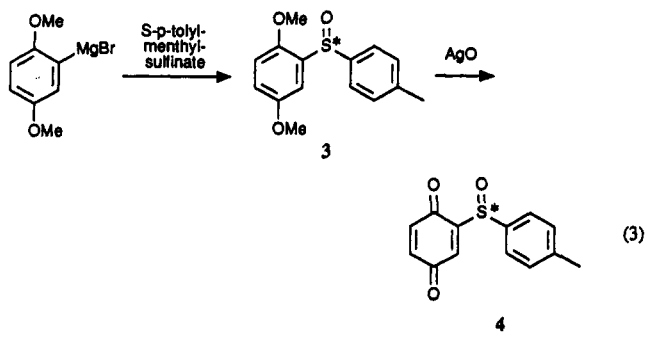
**Scheme I**




tolylsulfinyl benzoquinone 4 was prepared by a different route (eq 3).[10]




When the sulfinyl quinones **2a–c** and **4** were used as catalysts in the aerobic palladium-catalyzed 1,4-diacetoxylation of 1,3-cyclohexadiene, we observed not only a significant increase in the reaction rate compared to the sulfoxide-free reaction (Figure 1), but also a larger trans to cis product ratio. An experiment with catalytic amounts of an equimolar mixture of 1,4-hydroquinone (HQ) and dimethyl sulfoxide (DMSO) also yielded an improved reaction rate and stereoselectivity. This supports the assumption of a coordination of the sulfoxide.

In a semipreparative experiment with (phenylsulfinyl)benzoquinone (**2a**) as quinone catalyst, 5.2 mmol of 1,3-cyclohexadiene was oxidized aerobically to give an isolated yield of 85% of 1,4-diacetoxy-2-cyclohexene, (>95% trans) in 5.5 h. If, instead of **2a**, a catalytic amount of 1,4-hydroquinone is used with DMSO as cocatalyst the oxygen uptake ceased at 75% conversion and gave an isolated yield of diacetate of 72% (>95% trans) in 5.5 h.

**Table I. $^1$H NMR Chemical Shift Changes ($\Delta\delta$) of the ($\pi$-Allyl) Ligand Protons upon Addition of DMSO-$d_6$ to the Dimeric Bis[(4-acetoxy-$\eta^3$-(1,2,3)-cyclohexenyl)palladium acetate] (6) in Acetic Acid-$d_4$**

| | | | $\Delta\delta$ (Hz) | | | |
|---|---|---|---|---|---|---|
| complex | ligand, L | L:Pd | H-1 | H-2 | H-3 | H-4 |
| 6 | DMSO | 1.3:1 | 12 | 9 | 9 | |
| 6 | DMSO | 2.6:1 | 24 | 18 | 15 | |
| 6 | $CH_3CN$ | 2:1 | 9 | | 6 | -12 |
| 6 | $CH_3CN$ | 4:1 | 21 | | 15 | -18 |

In the presence of a sulfoxide-containing ligand the relative amount of trans product, resulting from internal attack of acetate (cis migration), was increased from 91% (10:1)[2] to >95% (20:1).

It has been shown by $^1$H NMR that the key step in the diacetoxylation is the coordination of the quinone to the ($\pi$-allyl)palladium complex.[11] When DMSO was added to the isolated intermediate ($\pi$-allyl)palladium complex **6**, significant alterations of the proton chemical shifts were observed (Table I). All the proton resonances were shifted to lower field and the line width of the signals decreased slightly. A similar but weaker effect was observed also for acetonitrile. These effects, which are not observed on addition of 1,4-benzoquinone only, indicate complexation of the sulfoxide and nitrile, respectively. No formation of diacetate could be detected as long as no benzoquinone was present.

These observations suggest that the sulfoxide, as the stronger ligand, is coordinated to palladium in the ($\pi$-allyl)palladium complex **5**, thus inhibiting the formation of the less reactive dimer **6**.[12] The rate of the reaction is

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(12) Since sulfoxides are strong bridge-splitting ligands,[6] the equilibrium is likely to favor the monomeric complex **5**.

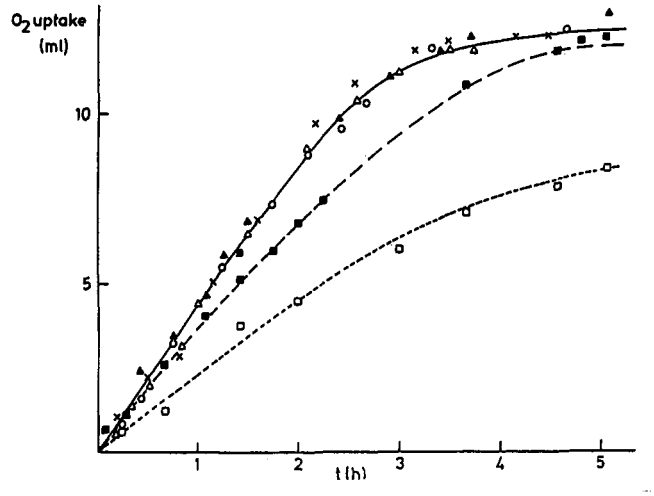
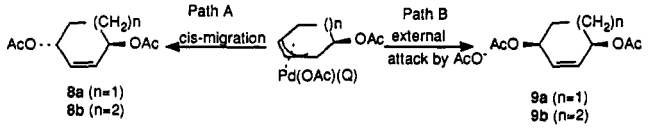



**Figure 1.** Oxygen uptake for the aerobic oxidation of 1 mmol of 1,3-cyclohexadiene catalyzed by the triple catalytic system $Pd(OAc)_2$–quinone–Fe(Pc) in acetic acid at room temperature (23 °C). Quinones used: x = **2a**, △ = **2b**, ○ = **2c**, ▲ = **4**, ■ = HQ + DMSO, □ = HQ.

**Scheme II**




further increased if the sulfoxide and the quinone are parts of the same molecule.

The improved stereoselectivity, which is a result of an increased rate of internal migration, indicates a specific interaction between ($\pi$-allyl)palladium complex, sulfoxide, and quinone. A probable reaction sequence is proposed in Scheme I.

Complex **5** with a sulfoxide coordinated should have a low reactivity toward nucleophiles compared to a ($\pi$-allyl)palladium–1,4-benzoquinone acetate complex, in accord with the inability of the analogous ($\pi$-allyl)palladium-(DMSO)–acetate complex to react with acetate in the absence of a quinone (vide supra). Coordination of the quinone double bond to palladium dramatically increases the reactivity. Such a coordination of **5** would lead to a highly reactive ($\sigma$-allyl)palladium complex **7** with palladium coordinated to the quinone double bond and probably also to the sulfoxide, which is known to be an ambidentate ligand.[13] We have previously reported results which indicate that cis migration of acetate takes place from a ($\sigma$-allyl)palladium complex.[2] The present results are consistent with a rate increase of internal cis migration (path A, Scheme II) by a factor of 2, whereas the rate of the external trans attack (path B) remains essentially the same. This would explain the change of the **8a**:**9a** ratio from 10:1 to 20:1 when 1,4-benzoquinone is replaced by a 2-sulfinyl-1,4-benzoquinone.

The proposed mechanism (Scheme I) was supported by the results from the sulfoxide-assisted diacetoxylation of 1,3-cycloheptadiene. When sulfinyl quinones were employed in the 1,4-diacetoxylation of 1,3-cycloheptadiene using the same reaction conditions as above, the reaction rate decreased considerably and the relative amount of *cis*-1,4-diacetoxy-2-cycloheptene (**9b**) decreased from 93% in the sulfoxide-free reaction[2] to 88%. Apparently the external attack by acetate (path B, Scheme II) has been slightly depressed. For steric reasons, the formation of a ($\sigma$-allyl)palladium complex and subsequent cis migration is unfavored in the seven-membered ring.[2] However, it is known that trans diacetoxylation of 1,3-cycloheptadiene is less unfavored at very low $AcO^-$ concentrations, e.g., no added LiOAc, and slightly elevated temperature (40 °C).[2] The presence of a sulfoxide under these reaction conditions increased the reaction rate slightly, but the stereochemistry of the product was not significantly changed from that obtained with 1,4-benzoquinone (i.e., **8b**:**9b** ≈ 2:1).

Since sulfoxides form strong complexes with palladium(II) salts[5] it occurred to us that the sulfoxide-containing quinone may be coordinated to palladium throughout the whole catalytic cycle (cf. Scheme I).[14] With a chiral sulfoxide this would result in a diastereomeric interaction in the coordination of the diene and hence in the formation of the ($\pi$-allyl)palladium complex. With the aim of obtaining asymmetric induction we therefore investigated the 1,4-diacetoxylation employing the enantiomerically pure sulfinyl quinone **4** as the ligand and electron-transfer mediator. However, no asymmetric induction has yet been detected.

## Conclusion

A sulfoxide as cocatalyst in the palladium-catalyzed diacetoxylation favors internal migration. For 1,3-cyclohexadienes, this results in an increase of the reaction rate and an increased trans diastereoselectivity. The results can be rationalized by a complexation of the sulfoxide to palladium and a subsequent formation of an intermediate ($\sigma$-allyl)palladium complex.

## Experimental Section

NMR spectra were recorded as follows: $^1H$ at 200 or 300 MHz and $^{13}C$ at 75.4 MHz. Spectra of 1,4-diacetates were recorded for $CDCl_3$ solutions. $^1H$ NMR spectra of ($\pi$-allyl)palladium complexes[15] were recorded for acetic acid-$d_4$ solutions. FT-IR spectra were recorded for $CDCl_3$ solutions. Mass spectra were recorded at 70 eV (direct inlet). Analytical gas chromatography was performed with a 30-m DB-5 J&M fused silica column. Palladium diacetate was from Aldrich. Fe(Pc) was either from Strem Chemicals Co. or synthesized as in ref 4c. Since Fe(Pc) has very low solubility in the reaction media, the degree of activity of the metal–macrocycle was important[16a] and the activity should be checked as described below for each batch used. 1,3-Cyclohexadiene was from Merck and was distilled prior to use.

**Test for the Catalytic Activity of Iron Phthalocyanine Fe(Pc).** A solution of 70 mg (0.12 mmol, 5%) of Fe(Pc) and 250 mg of hydroquinone (2.27 mmol) in 5 mL HOAc was stirred under an $O_2$ atmosphere. The $O_2$ consumption was followed with a buret.[4b,c] Fe(Pc) with acceptable to good catalytic activity should consume 27 mL of $O_2$ in 6–10 h ($T_{1/2}$ = 2–3 h), whereas some very active batches were able to complete the oxidation in 2 h ($T_{1/2}$ = 30 min).

**Activation of Fe(Pc).**[16] Inactive Fe(Pc) (2 g) was dissolved in 50 mL of concentrated $H_2SO_4$. The brown solution was filtered in contact with air, and Fe(Pc) was precipitated by carefully pouring the acidic solution into 300 mL of cold aqueous EtOH (30% v/v). The mixture was allowed to cool to rt. The green suspension of Fe(Pc) was centrifuged, and the pellet was washed

(13) Complexes where sulfoxides act as ambidentate ligands to palladium have been isolated[5c] and characterized.[5b,c]

(14) Equimolar amounts of $Pd(OAc)_2$ and sulfinyl quinone **2a** in acetic acid formed a precipitate which, according to MS and IR, contained palladium and quinone. The stoichiometry and structure of the complex are currently under investigation.

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with water (three times), very dilute $NH_4OH$, and finally once with water. The Fe(Pc) was then dried over $P_2O_5$ in vacuo to yield about 0.8 g of activated Fe(Pc), which was then checked as described above. Active Fe(Pc) should be kept in dark containers.

**General Procedure for the Preparation of Racemic Sulfinyl Quinones. (I) Preparation of 2-(Arylthio)- and 2-(Alkylthio)-1,4-quinones. 2-(Phenylthio)-1,4-benzoquinone (1a).**[9a,b] Thiophenol (5 mL, 0.04 mol) in methanol (5 mL) was added to a suspension of 1,4-benzoquinone (8.7 g, 0.081 mol) in methanol (50 mL). The mixture was swirled for 5 min, during which time it became a clear, orange-brown solution. Water (100 mL) was added, and the resulting precipitate was collected by filtration. The orange crystals were recrystallized from cyclohexane to yield 5.8 g (69%) of the thioether **1a**: mp 113–115 °C (lit.[9b] mp 114 °C); $^1H$ NMR $\delta$ 7.5 (s, 5 H, phenyl), 6.82 (d, $J$ = 13 Hz, 1 H, H-6), 6.68 (d, $J$ = 13 Hz, 1 H, H-5), 5.88 (s, 1 H, H-3); IR 1668, 1644, 1567 $cm^{-1}$; MS $m/z$ 216 ($M^+$, 56), 187 (20), 160 (17), 134 (85).

**2-(Cyclohexylthio)-1,4-benzoquinone (1b)** was prepared according to the above procedure. **1b** was isolated in 83% yield as orange-brown crystals: mp 102–106 °C; $^1H$ NMR $\delta$ 6.8 (d, $J$ = 10 Hz, 1 H, H-6), 6.72 (dd, $J$ = 10, 3 Hz, 1 H, H-5), 6.41 (d, $J$ = 3 Hz, 1 H, H-3), 3.1 (tt, $J$ = 4, 10 Hz, 1 H, S-CH), 2.05 (m, 2 H), 1.81 (m, 2 H), 1.45 (m, 6 H); IR 1667, 1642, 1546 $cm^{-1}$; MS $m/z$ 222 ($M^+$, 14), 142 (28), 112 (7). Anal. Calcd for $C_{12}H_{14}O_2S$: C 64.83; H 6.36. Found: C, 64.64; H 6.18.

**2-($n$-Butylthio)-1,4-benzoquinone (1c)**[9c] was prepared as described above. **1c** was obtained as red-brown crystals in 55% yield: mp 78–80 °C (lit.[9c] mp 82 °C); $^1H$ NMR $\delta$ 6.8 (d, $J$ = 10 Hz, 1 H, H-6), 6.71 (dd, $J$ = 3, 10 Hz, 1 H, H-5), 6.38 (d, $J$ = 3 Hz, 1 H, H-3), 2.77 (t, $J$ = 7 Hz, 2 H, S-$CH_2$), 1.72 and 1.48 (two m, $w_{1/2}$ = 9 Hz, 2 H each, $CH_2$), 0.96 (t, $J$ = 7 Hz, 3 H, $CH_3$); IR 1668, 1643, 1547 $cm^{-1}$; MS $m/z$ 196 ($M^+$, 29), 140 (49), 112 (37), 82 (42).

**(II) Preparation of 2-Sulfinyl-1,4-quinones. 2-(Phenylsulfinyl)-1,4-benzoquinone (2a).**[9a] To a solution of the thioether (1.0 g, 0.05 mol) in $CH_2Cl_2$ (20 mL) was added $m$-chloroperoxybenzoic acid ($m$-CPBA) (1.1 equiv) in $CH_2Cl_2$ (5 mL). The mixture was stirred at rt for 1 h. The mixture was then washed with aqueous saturated $NaHCO_3$ (3 × 10 mL), dried ($MgSO_4$), and evaporated to give 0.9 g of crude product, which was flash chromatographed (silica, $CH_2Cl_2$–ether gradient) to yield the phenylsulfinyl quinone **2a** (0.75 g, 70%) as orange needles: mp 118 °C (lit.[9a] mp 118.5–119.5 °C); $^1H$ NMR $\delta$ 7.78 (m, 2 H, phenyl), 7.5 (m, 3 H, phenyl), 7.44 (d, $J$ = 2 Hz, 1 H, H-3), 6.81 (dd, $J$ = 10, 2 Hz, 1 H, H-5), 6.72 (d, $J$ = 10 Hz, 1 H, H-6); IR 1666, 1098 $cm^{-1}$; MS $m/z$ 232 ($M^+$, 23), 184 (9), 150 (27).

**2-(Cyclohexylsulfinyl)-1,4-benzoquinone (2b)** was isolated in 86% yield as orange needles, mp 112–113 °C, after stirring the thioether **1b** with 1.1 equiv of $m$-CPBA in $CH_2Cl_2$ for 12 min at 0 °C and subsequent workup as described above: $^1H$ NMR $\delta$ 7.22 (d, $J$ = 2 Hz, 1 H, H-3), 6.72 (br s, 2 H, H-5 and H-6), 2.95 (tt, $J$ = 4, 12 Hz, 1 H, SCH), 2.15–1.2 (several m, 10 H); IR 1663, 1586, 1065 $cm^{-1}$; MS $m/z$ 156 ($M^+ - C_6H_{10}$, 27), 112 (2.5), 83 (45), 55 (100). Anal. Calcd for $C_{12}H_{14}O_3S$: C 60.47; H 5.93. Found: C 60.39; H 5.88.

**2-($n$-Butylsulfinyl)-1,4-benzoquinone (2c)** was obtained in 50% yield as orange crystals, mp 65–71 °C, after stirring the thioether **1c** with 1.1 equiv of $m$-CPBA in $CH_2Cl_2$ for 10 min at 0 °C and subsequent workup as described above: $^1H$ NMR $\delta$ 7.3 (d, $J$ = 2 Hz, 1 H, H-3), 6.88 (br s, 2 H, H-5 and H-6), 3.13 and 2.84 (two m, $w_{1/2}$ = 11 Hz, 1 H each, $SCH_2$), 1.9 and 1.58 (two m, $w_{1/2}$ = 27 Hz, 1 H each, $SCCH_2$), 1.47 (m, $w_{1/2}$ = 23 Hz, 2 H), 0.96 (t, $J$ = 6.5 Hz, 3 H, $CH_3$); IR 1663, 1047 $cm^{-1}$; MS $m/z$ 163 (18), 156 ($M^+ - C_4H_8$, 43), 139 (16), 128 (3), 82 (11). Anal. Calcd for $C_{10}H_{12}O_3S$: C, 56.58; H. 5.71. Found: C, 56.43; H, 5.56.

**Preparation of Optically Active Sulfinyl Quinone. 1-($R$)-(+)-($p$-Tolylsulfinyl)-2,5-dimethoxybenzene (3).**[10a] 1-Bromo-2,5-dimethoxybenzene (1.0 g, 4.6 mmol) in dry THF (4 mL) was added to dry Mg (0.15 g, 6.4 mmol), and the mixture was stirred under $N_2$. The reaction started on heating. The Grignard reagent formed was added slowly (1.5 h) with a syringe to a solution of (S)-(−)-($p$-tolylmenthyl)sulfinate (1.36 g, 4.6 mmol) in diethyl ether (10 mL) at 0 °C under $N_2$. The reaction was stirred at 0 °C for an additional 3.5 h, then at rt for 3 h. At 50% conversion (GC) the reaction was washed with aqueous saturated $NH_4Cl$ (3 × 100 mL) and the organic layer was collected. The aqueous layer was extracted with ether (3 × 15 mL). The combined organic layers were dried ($MgSO_4$) and concentrated to 3 mL. The crude product was then flash chromatographed (silica, ether) and evaporated to yield 0.43 g (65% based on reacted material) of **3** as beige crystals, mp 84–88 °C, and unreacted chiral ($p$-tolylmenthyl)sulfinate. $^1H$ NMR of **3**: $\delta$ 7.58 and 7.22 (AA'XX', 4 H, tolyl system), 7.49 (d, $J$ = 3 Hz, 1 H, H-6), 6.91 (dd, $J$ = 9, 3 Hz, 1 H, H-4), 6.78 (d, $J$ = 9 Hz, 1 H, H-3), 3.83 and 3.72 (two s, 3 H each, OMe), 2.35 (s, 3 H, ArMe); IR 1493, 1042 $cm^{-1}$; MS $m/z$ 276 ($M^+$, 36), 259 (74), 228 (37), 198 (15), 105 (100).

**($R$)-(+)-1-($p$-Tolylsulfinyl)-2,5-benzoquinone (4).**[10a] Protected quinone **3** (99 mg, 0.4 mmol) and freshly prepared AgO (200 mg, 1.6 mmol) were mixed in 4 mL of dry dioxane. $HNO_3$ (6 M, 0.4 mL) was added, and the mixture was stirred in air at room temperature for 5 min, during which time the mixture turned red and cleared. The reaction was quenched by the addition of water (4 mL) and $CHCl_3$ (16 mL). The organic layer was washed with water (2 × 5 mL), dried ($Na_2SO_4$), and evaporated. The crude product was recrystallized from ether to yield 90 mg (91%) of **4** as red needles, mp 129 °C. Physical and spectroscopic properties were in accordance with the literature.[10a]

**General Procedure for Sulfoxide-Assisted Palladium(II)-Catalyzed 1,4-Diacetoxylation of Conjugated Dienes. 1,4-Diacetoxy-2-cyclohexene. Use of Sulfinyl Quinones.** $Pd(OAc)_2$ (51 mg, 0.23 mmol), (phenylsulfinyl)benzoquinone (**2a**; 61 mg, 0.27 mmol), Fe(Pc) (50 mg, 0.09 mmol), and $LiOAcx2H_2O$ (635 mg, 6 mmol) were dissolved in acetic acid (10.0 mL). The reaction vessel was quickly purged with 1 atm of $O_2$.[4b,c] 1,3-Cyclohexadiene (419 mg, 5.2 mmol) was added over a period of 2 h. The oxygen consumption was monitored with a gas buret.[4b] When the consumption had ceased (61 mL (2.5 mmol) of $O_2$, 5 h 30 min), the reaction mixture was worked up by first diluting it to 30 mL with water, followed by extraction (4 × 15 mL pentane/ether (4:1)). The combined organic layers were washed (1 × 15 mL of $H_2O$; 2 × 15 mL of 2 M NaOH; 1 × 15 mL of $H_2O$), dried ($MgSO_4$), and evaporated to yield 875 mg (4.4 mmol, 85%) of 1,4-diacetoxy-2-cyclohexene, >95% trans (±0.5% from $^1H$ NMR), as white crystals. The product was compared (NMR) with an authentic sample.[2]

**Use of DMSO.** As described above for the (phenylsulfinyl)benzoquinone, but replacing the sulfinyl quinone with 1,4-hydroquinone (29 mg, 0.27 mmol). After the first addition of diene (total 420 mg, 5.2 mmol), 20 $\mu$L (0.28 mmol) of DMSO was added. After 5 h 30 min the oxygen uptake had ceased (46 mL, 1.9 mmol of $O_2$). Subsequent workup yielded 745 mg (3.8 mmol, 72%) of 1,4-diacetoxy-2-cyclohexene, >95% trans (±0.5% from $^1H$ NMR).

Capillary GC of the organic layer before the washing procedure indicated that some quinone had been consumed in a Diels–Alder reaction with 1,3-cyclohexadiene.

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**Registry No.** **1a**, 18232-03-6; **1b**, 135615-63-3; **1c**, 18232-09-2; (±)-**2a**, 135615-64-4; (±)-**2b**, 135615-65-5; (±)-**2c**, 135615-66-6; **3**, 135615-67-7; **4**, 135615-68-8; **6**, 135619-93-1; (±)-*trans*-**8a**, 135615-69-9; HQ, 123-31-9; DMSO, 67-68-5; $Pd(OAc)_2$, 3375-31-3; Fe(Pc), 132-16-1; BuSH, 109-79-5; 1,4-benzoquinone, 106-51-4; thiophenol, 108-98-5; cyclohexanethiol, 1569-69-3; 1-bromo-2,5-dimethoxybenzene, 25245-34-5; (S)-(-)-menthyl $p$-tolylsulfinate, 1517-82-4; 1,3-cyclohexadiene, 592-57-4.