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2-ALKYLIDENE-1,3-DITHIANE MONOXIDES AS ACTIVATED ALKENES IN RHODIUM-CATALYZED ADDITION REACTION OF ARYLBORONIC ACIDS

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Abstract – 2-Methylene-1,3-dithiane 1-oxide reacts with arylboronic acids in the presence of a rhodium catalyst in aqueous dioxane to afford 2-arylmethyl-1,3-dithiane 1-oxides in good yields.

INTRODUCTION

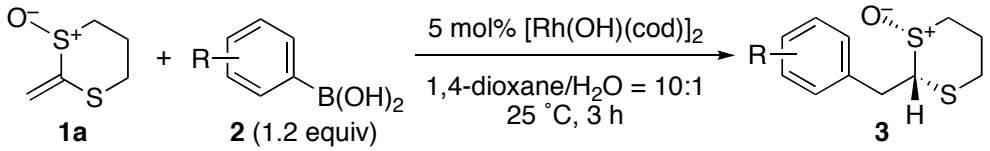
Ketene dithioacetal and its derivatives are useful two-carbon building blocks as ketene equivalents in organic synthesis.[1] We have been interested in their utility,[2] and recently disclosed that ketene dithioacetal monoxides serve as activated alkenes in rhodium-catalyzed addition of arylboronic acids.[3,4] Rhodium-catalyzed 1,4-additions of arylboronic acids to α,β-unsaturated carbonyl compounds are extensively studied.[5] On the other hand, the reactions of heteroatom-substituted electron-deficient alkenes are still unexplored.[6] In light of the importance of the rhodium-catalyzed addition of organoboron compounds, we report herein full details about the rhodium-catalyzed addition of arylboronic acids to ketene dithioacetal monoxides.

RESULTS AND DISCUSSION

Treatment of 2-methylene-1,3-dithiane 1-oxide (**1a**) with phenylboronic acid (**2a**, 1.2 equiv) in the presence of $[Rh(OH)(cod)]_2$ (5 mol%, COD = 1,5-cyclooctadiene) in aqueous dioxane at 25 ˚C for 3 h provided the corresponding adduct **3a** in 97% yield (Table 1, entry 1). The reaction afforded the *cis* isomer, which is a known compound,[7] exclusively, and the *trans* isomer of **3a** was not detected. A variety of arylboronic acids participated in the reaction. The electronic nature of the substituents of

arylboronic acids proved to have little influence on the efficiency of the reactions (entries 2–5). Sterically demanding *ortho*-substituted arylboronic acids **2f** and **2g** added to **1a** under the rhodium catalysis to yield the corresponding adducts in excellent yields (entries 6 and 7). Although alkenylboronic acid **2h** was less reactive, use of an excess of 1,5-cyclooctadiene and a larger amount of the rhodium complex led to a satisfactory yield (Equation 1).

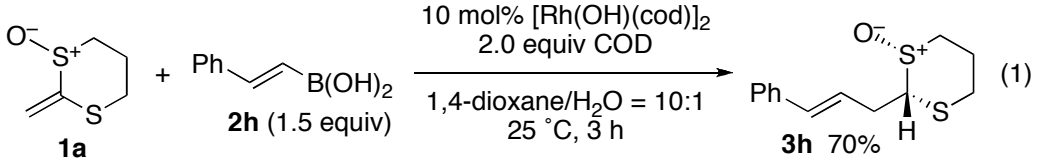
Table 1. Rhodium-Catalyzed Arylation of **1a** with Various Arylboronic Acids



1a + **2** (1.2 equiv) → **3**

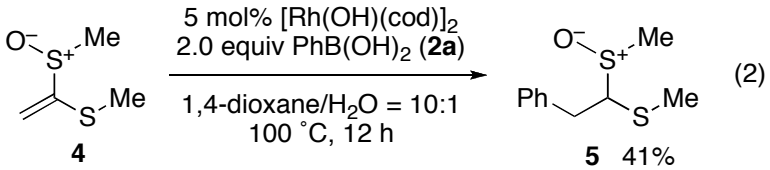
entry	R	2	3	yield (%)
1	H	**2a**	**3a**	97
2	4-MeO	**2b**	**3b**	89
3	4-Me	**2c**	**3c**	89
4	4-CF_3	**2d**	**3d**	>99
5	4-MeOOC	**2e**	**3e**	90
6	2-MeO	**2f**	**3f**	96
7	2-BocNH[a]	**2g**[b]	**3g**	96

[a] Boc = *t*-BuOC(=O). [b] Two equivalents of **2g** were used.



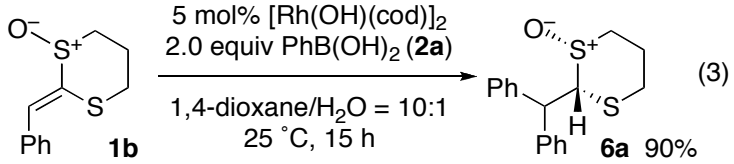
1a + **2h** (1.5 equiv) → **3h** 70% (1)

It is worth noting that acyclic ketene dithioacetal monoxide **4** was the less reactive Michael acceptor than cyclic **1a** (Equation 2). Addition of **2a** to **4** furnished **5** in only 41% yield, and 40% of **4** was recovered even at an elevated temperature and with an excess of **2a**. The reaction of **4** provided a 6:4 (determined by ^{1}H NMR) separable mixture of stereoisomers, which is different from the reaction of **1a**.



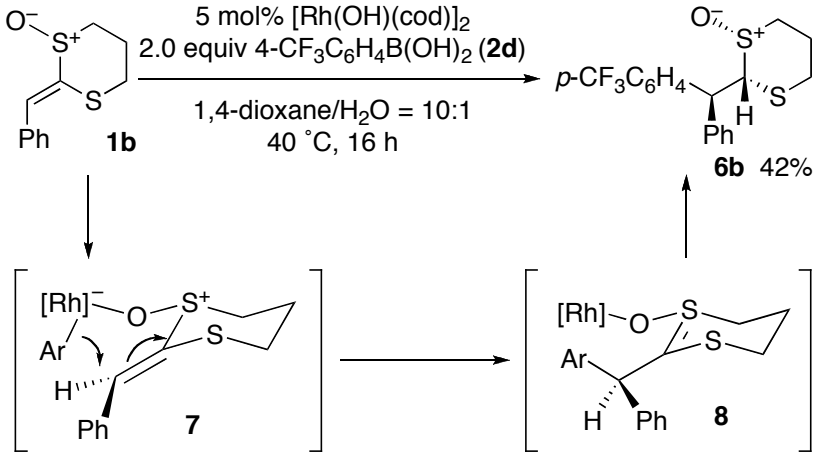
4 → **5** 41% (6:4 mixture of diastereomers) + **4** 40% recovery (2)

Phenyl-substituted **1b** was less reactive because of the steric hindrance of the phenyl group. Although the phenylation reaction of **1b** required a longer reaction time and two equivalents of phenylboronic acid, the reaction afforded the corresponding product **6a** in high yield with exclusive stereoselectivity (Equation 3).



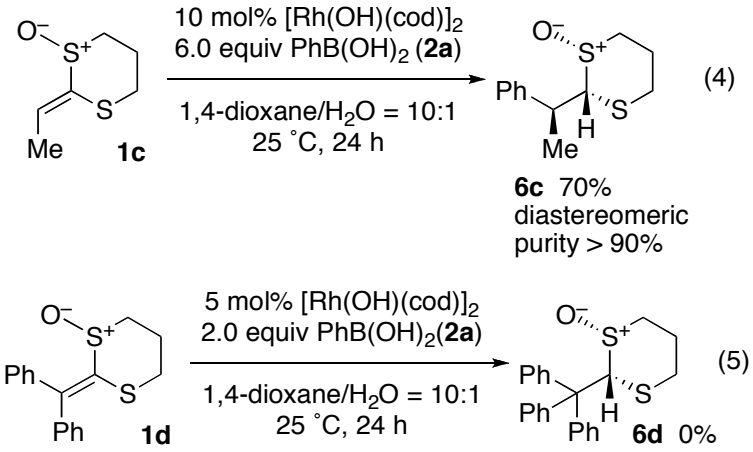
(3)

The reaction of **1b** with arylboronic acid **2d** yielded **6b** with high diastereoselectivity (Scheme 1). The relative stereochemistry of **6b** was unambiguously determined by X-ray crystallographic analysis. Based on the configuration of **6b**, we are tempted to assume the reaction mechanism as follows. Arylrhodium, generated by transmetalation between **2d** and the rhodium catalyst, would be coordinated by the oxygen of **1b** to form **7**. The aryl group on the rhodium would attack to the activated double bond in a diastereoface-selective fashion to yield **8**.[8] Protonation of **8** would take place from the same side where the aryl group would have attacked, affording **6b** selectively.

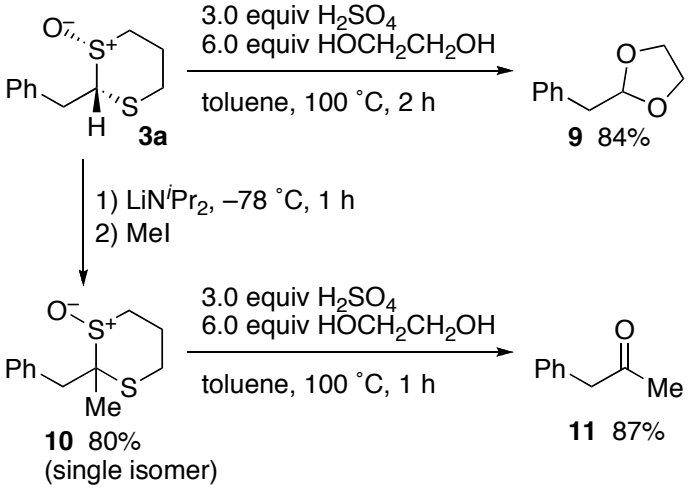


Scheme 1. The Reaction Mechanism of the Diastereoselective Arylation of **1b** with **2d**

The reaction of **1c** required a large excess of phenylboronic acid, a larger amount of $[Rh(OH)(cod)]_2$, and a prolonged reaction time to proceed to completion (Equation 4). Product **6c** was contaminated with a small amount of a stereoisomer, the relative configuration of which we were unable to assign. Unfortunately, *gem*-diphenyl-substituted 2-alkylidene-1,3-dithiane 1-oxide **1d** resisted the reaction (Equation 5).



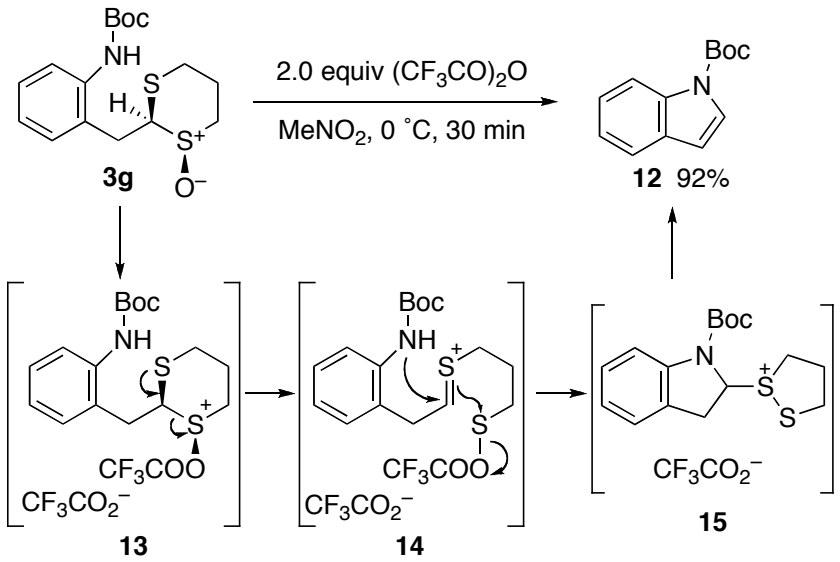
The products **3** and **6** are useful building blocks as 2-arylalkanal equivalents. However, a number of attempts to convert **3a** to phenylacetaldehyde resulted in either formation of a complex mixture or no conversion. The failure would be due to the instability of phenylacetaldehyde under strongly acidic or basic conditions. Instead, treatment of **3a** with ethylene glycol in the presence of sulfuric acid in toluene at 100 °C provided 2-benzyl-1,3-dioxolane (**9**) in 84% yield (Scheme 2).[9] Deprotonation of **3a** with lithium diisopropylamide followed by addition of iodomethane afforded a methylated product **10** in good yield.[10] Intriguingly, attempted acetalization of **10** with ethylene glycol unexpectedly furnished benzyl methyl ketone (**11**) in high yield.



Scheme 2. Transformation of **3a**

Treatment of **3g** with trifluoroacetic anhydride in nitromethane provided *N*-Boc-protected indole **12** in excellent yield (Scheme 3). The trifluoroacetylation of the sulfoxide followed by the cleavage of the carbon-sulfur bond[11] would afford a cationic intermediate **14**. Intramolecular nucleophilic attack of the Boc-protected amino group led to ring closure to yield dihydroindole **15** with concomitant liberation of

trifluoroacetate. Elimination of dithiacyclopentane yielded **12**. The series of the transformations from **1a** is a new method for constructing indole skeletons.



Scheme 3. Synthesis of Boc-Protected Indole **12** from **3g**

EXPERIMENTAL

Instrumentation and Chemicals

^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were taken on Varian UNITY INOVA 500 spectrometers and were recorded in $CDCl_3$. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^{1}H and relative to $CDCl_3$ at 77.23 ppm for ^{13}C unless otherwise noted. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. X-ray crystal structure analysis was carried out with a Bruker SMART APEX CCD diffractometer with Mo-K_α radiation. The structure was solved by direct methods and refined by full-matrix least squares methods on F^2 with the SHELXL-97. Mass spectra (EI unless otherwise noted) were determined on a JEOL MStation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. The rhodium catalyst was prepared according to the literature.[12] Dioxane was purchased from Wako Pure Chemical and dried over slices of sodium. Distilled water was used for the addition reaction. Substrate **1** were prepared according to the literature.[13] Most of arylboronic acids **2** were purchased from Wako Pure Chemical. Arylboronic acid **2g** was prepared according to the literature.[14] All reactions were carried out under argon atmosphere.

Typical Procedure for Rhodium-Catalyzed Addition Reaction (Table 1, entry 1): $[Rh(OH)(cod)]_2$ (7.3 mg, 0.016 mmol) was placed in a 20-mL reaction flask under argon. Water (0.30 mL) and a solution of 2-methylene-1,3-dithiane 1-oxide (**1a**, 44.1 mg, 0.30 mmol) in dioxane (3.0 mL) were added. Phenylboronic acid (**2a**, 43.8 mg, 0.36 mmol) was added, and the resulting mixture was stirred at 25 ˚C for 3 h. The mixture was poured into saturated aqueous $NaHCO_3$ (5 mL) and extracted with EtOAc (10 mL × 3). The combined organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. Chromatographic purification on silica gel yielded 2-benzyl-1,3-dithiane 1-oxide (**3a**, 65.6 mg, 0.29 mmol, 97%).

Transformation of 3a to 9: A toluene (3.0 mL) solution of 1,2-*cis*-2-benzyl-1,3-dithiane 1-oxide (**3a**, 69.3 mg, 0.30 mmol) was placed in a flask under an atmosphere of argon. Then, ethylene glycol (0.10 mL, 1.8 mmol) and sulfuric acid (0.050 mL, 0.94 mmol) were added and the mixture was stirred at 100 ˚C for 2 h. The reaction mixture was poured into saturated aqueous $NaHCO_3$ (5 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. Purification by chromatography on silica gel provided 2-benzyl-1,3-dioxolane (**9**, 42.0 mg, 84%).

Transformation of 3a to 11: A THF (2.0 mL) solution of diisopropylamine (0.052 mL, 0.37 mmol) was placed in a flask under an atmosphere of argon. Then, butyllithium in hexane (1.6 M, 0.22 mL, 0.36 mmol) was added at 0 ˚C, and the resulting mixture was stirred for 10 min at the same temperature. The mixture was added to a THF (3.0 mL) solution of 1,2-*cis*-2-benzyl-1,3-dithiane 1-oxide (**3a**, 61.3 mg, 0.27 mmol) at –78 ˚C, and the resulting mixture was stirred for 1 h at the same temperature. Iodomethane (0.037 mL, 0.59 mmol) was then added, and the reaction was allowed to warm to rt gradually over 2 h. The reaction mixture was poured into saturated aqueous NH_4Cl (5 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. Chromatographic purification on silica gel afforded 2-benzyl-2-methyl-1,3-dithiane 1-oxide (**10**, 52.1 mg, 0.22 mmol, 80%).

A toluene (3.0 mL) solution of 2-benzyl-2-methyl-1,3-dithiane 1-oxide (**10**, 58.7 mg, 0.26 mmol) was placed in a flask under an atmosphere of argon. Ethylene glycol (0.10 mL, 1.8 mmol) and sulfuric acid (0.050 mL, 0.94 mmol) were added and the mixture was stirred at 100 ˚C for 1 h. The reaction mixture was poured into saturated aqueous $NaHCO_3$ (5 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. Silica gel column purification provided 1-phenyl-2-propanone (**11**, 28.4 mg, 0.21 mmol, 87%).

Synthesis of Boc-Protected Indole 12: A nitromethane (4.0 mL) solution of 1,2-*cis*-2-[2-(*tert*-butoxycarbonylamino)phenylmethyl]-1,3-dithiane 1-oxide (**3g**, 70.3 mg, 0.21 mmol) was placed in a flask under an atmosphere of argon. Then, trifluoroacetic anhydride (0.057 mL, 0.41

mmol) was added at 0 ˚C, and the resulting mixture was stirred for 30 min at the same temperature. The reaction mixture was poured into saturated aqueous $NaHCO_3$ (5 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. Purification by chromatography on silica gel provided *N-tert*-butoxycarbonylindole (**12**, 41.2 mg, 0.19 mmol, 92%).

Characterization Data of Compounds

Compounds **1a**,[4] **3a**,[7] **3h**,[15] and **4**[16] showed the identical spectra reported in the literature. The ^{1}H NMR spectra of **9** and **12** are identical to the corresponding commercially available compounds.

(*E*)-2-(benzylidene)-1,3-dithiane 1-oxide (1b): Mp 67–68 ºC (hexane/EtOAc); IR (Nujol) 2923, 2854, 1559, 1457, 1057, 752 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.50–2.67 (m, 3H), 2.84–2.92 (m, 2H), 3.42–3.46 (m, 1H), 7.35–7.38 (m, 1H), 7.39–7.44 (m, 2H), 7.53 (s, 1H), 7.77–7.79 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 27.3, 32.0, 55.2, 128.6, 129.4, 130.3, 133.9, 134.7, 137.0. Anal. Calcd for $C_{11}H_{12}OS_2$: C, 58.89; H, 5.39%. Found: C, 58.84; H, 5.35%.

(*E*)-2-ethylidene-1,3-dithiane 1-oxide (1c): Mp 41–42 ºC (hexane/EtOAc); IR (Nujol) 2923, 2854, 1609, 1457, 1429, 1373, 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.03 (d, J = 7.0 Hz, 3H), 2.35–2.45 (m, 1H), 2.52–2.62 (m, 2H), 2.66–2.77 (m, 2H), 3.25–3.32 (m, 1H), 6.74 (q, J = 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.8, 26.8, 31.4, 54.7, 134.4, 137.2. Anal. Calcd for $C_6H_{10}OS_2$: C, 44.41; H, 6.21%. Found: C, 44.16; H, 6.20%.

2-(diphenylmethylene)-1,3-dithiane 1-oxide (1d): Mp 203–204 ºC (hexane/EtOAc); IR (Nujol) 2924, 2854, 1559, 1457, 1052, 1043 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.94–1.98 (m, 1H), 2.75–2.79 (m, 1H), 2.84–2.90 (m, 1H), 2.94–3.05 (m, 2H), 3.16–3.20 (m, 1H), 7.14–7.16 (m, 2H), 7.20–7.22 (m, 2H), 7.34–7.39 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 15.4, 30.8, 48.1, 128.3, 128.4, 129.0, 129.0, 130.0, 130.3, 136.5, 139.1, 139.7, 153.5. Anal. Calcd for $C_{17}H_{16}OS_2$: C, 67.96; H, 5.37%. Found: C, 67.94; H, 5.46%.

1,2-*cis*-2-(4-methoxyphenylmethyl)-1,3-dithiane 1-oxide (3b): Mp 112–113 ºC (hexane/EtOAc); IR (Nujol) 2923, 2854, 1610, 1513, 1456, 1247, 1057 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.99–2.06 (m, 1H), 2.48–2.55 (m, 1H), 2.60–2.72 (m, 3H), 2.92 (dd, J = 5.5, 14.5 Hz, 1H), 3.00–3.08 (m, 1H), 3.34 (dd, J = 9.0, 14.5 Hz, 1H), 3.80 (s, 3H), 3.84 (dd, J = 3.0, 9.0 Hz, 1H), 6.86–6.89 (m, 2H), 7.20–7.23 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.8, 26.1, 31.6, 46.2, 55.5, 61.1, 114.3, 128.7, 130.7, 159.0. Anal. Calcd for $C_{12}H_{16}O_2S_2$: C, 55.93; H, 6.00%. Found: C, 56.22; H, 6.29%.

1,2-*cis*-2-(4-tolylmethyl)-1,3-dithiane 1-oxide (3c): Mp 113–114 ºC (hexane/EtOAc); IR (Nujol) 2923, 2854, 1460, 1051, 994, 811 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.96–2.08 (m, 1H), 2.34 (s, 3H), 2.48–2.55 (m, 1H), 2.59–2.64 (m, 1H), 2.68–2.72 (m, 2H), 2.93 (dd, J = 5.0, 14.0 Hz, 1H), 3.00–3.05 (m, 1H), 3.37 (dd, J = 9.0, 13.5 Hz, 1H), 3.86 (dd, J = 3.0, 9.0 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H);

^{13}C NMR ($CDCl_3$) δ 21.1, 21.3, 26.0, 32.0, 46.2, 60.9, 129.6, 129.6, 133.8, 137.0. Anal. Calcd for $C_{12}H_{16}OS_2$: C, 59.96; H, 6.71%. Found: C, 59.86; H, 6.62%.

1,2-*cis*-2-(4-trifluoromethylphenylmethyl)-1,3-dithiane 1-oxide (3d): Mp 130–131 ºC (hexane/EtOAc); IR (Nujol) 2923, 2854, 1327, 1158, 1106, 1044 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.04–2.11 (m, 1H), 2.49–2.55 (m, 1H), 2.59–2.63 (m, 1H), 2.70–2.80 (m, 2H), 2.96–3.04 (m, 2H), 3.50 (dd, *J* = 9.0, 14.0 Hz, 1H), 3.87 (dd, *J* = 4.5, 9.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.8, 25.6, 31.7, 46.3, 60.0, 124.3 (q, *J* = 270 Hz), 125.8 (q, *J* = 3.4 Hz), 129.8 (q, *J* = 32 Hz), 130.1, 141.2. Anal. Calcd for $C_{12}H_{13}F_3OS_2$: C, 48.96; H, 4.45%. Found: C, 48.81; H, 4.41%.

1,2-*cis*-2-(4-methoxycarbonylphenylmethyl)-1,3-dithiane 1-oxide (3e): Mp 108–109 ºC (hexane/EtOAc); IR (Nujol) 2922, 2854, 1718, 1437, 1285, 1044, 753 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.05–2.10 (m, 1H), 2.49–2.56 (m, 1H), 2.59–2.64 (m, 1H), 2.70–2.80 (m, 2H), 3.00–3.05 (m, 2H), 3.50 (dd, *J* = 9.0, 14.0 Hz, 1H), 3.90 (dd, *J* = 4.0, 9.0 Hz, 1H), 3.92 (s, 3H), 7.37–7.39 (m, 2H), 8.01–8.03 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.8, 25.7, 31.9, 46.3, 52.3, 60.1, 129.4, 129.8, 130.2, 142.4, 167.0. Anal. Calcd for $C_{13}H_{16}O_3S_2$: C, 54.90; H, 5.67%. Found: C, 54.78; H, 5.64%.

1,2-*cis*-2-(2-methoxyphenylmethyl)-1,3-dithiane 1-oxide (3f): Mp 81–82 ºC (hexane/EtOAc); IR (Nujol) 2923, 2854, 1586, 1496, 1244, 1020, 755 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.95–2.00 (m, 1H), 2.48–2.55 (m, 1H), 2.59–2.72 (m, 3H), 3.01–3.08 (m, 2H), 3.37 (dd, *J* = 8.5, 14.0 Hz, 1H), 3.85 (s, 3H), 4.07 (dd, *J* = 3.0, 8.5 Hz, 1H), 6.88–6.94 (m, 2H), 7.22 (dd, *J* = 6.0, 8.0 Hz, 1H), 7.27 (ddd, *J* = 2.0, 8.0, 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.3, 26.4, 28.3, 46.2, 55.6, 58.9, 110.7, 120.7, 124.8, 128.8, 131.8, 157.9. Anal. Calcd for $C_{12}H_{16}O_2S_2$: C, 56.22; H, 6.29%. Found: C, 55.95; H, 6.38%.

1,2-*cis*-2-[2-(*tert*-butoxycarbonylamino)phenylmethyl]-1,3-dithiane 1-oxide (3g): Mp 57–58 ºC (hexane/EtOAc); IR (Nujol) 2923, 2854, 1717, 1452, 1158, 1024 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.53 (s, 9H), 2.04–2.15 (m, 1H), 2.45–2.54 (m, 1H), 2.61–2.69 (m, 1H), 2.71–2.84 (m, 2H), 2.94–3.03 (m, 2H), 3.44 (dd, *J* = 6.0, 14.5 Hz, 1H), 3.85 (dd, *J* = 6.0, 6.0 Hz, 1H), 7.08 (ddd, *J* = 3.5, 7.0, 7.0 Hz, 1H), 7.25–7.31 (m, 2H), 7.49 (br s, 1H), 7.79 (d, *J* = 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 22.4, 25.5, 28.2, 28.6, 45.7, 58.9, 80.5, 123.9, 124.5, 128.1, 128.4, 130.8, 136.9 154.1. HRMS (*m*/*z*) Calcd for $C_{16}H_{23}O_3NS_2$: 341.1119. Observed: 341.1120.

1-methylsulfinyl-1-methylthio-2-phenylethane (5): The major isomer: oil. ^{1}H NMR ($CDCl_3$) δ 2.17 (s, 3H), 2.64–2.69 (m, 4H), 3.65–3.70 (m, 2H), 7.27–7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 16.2, 31.3, 32.3, 67.4, 127.2, 128.9, 129.6, 137.5. The minor isomer: oil. ^{1}H NMR ($CDCl_3$) δ 2.15 (s, 3H), 2.78 (s, 3H), 2.85 (dd, *J* = 11.0, 14.0 Hz, 1H), 3.54 (dd, *J* = 3.5, 14.0 Hz, 1H), 3.69 (dd, *J* = 3.5, 11.0 Hz, 1H), 7.27–7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.3, 33.7, 36.9, 69.7, 127.3, 128.9, 129.5, 137.0. Anal. Calcd for $C_{10}H_{14}OS_2$: C, 56.03; H, 6.58%. Found: C, 56.28; H, 6.48%.

(1*R,2*S**)-2-(diphenylmethyl)-1,3-dithiane 1-oxide (6a):** Mp 188–189 ºC (hexane/EtOAc); IR (Nujol) 2923, 2854, 1457, 1044, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.74–1.80 (m, 1H), 2.41–2.60 (m, 3H), 2.84–2.90 (m, 1H), 3.10–3.14 (m, 1H), 4.23 (d, *J* = 12.5 Hz, 1H), 4.46 (d, *J* = 12.5, Hz, 1H), 7.22–7.42 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 14.1, 29.3, 46.5, 52.6, 65.4, 127.4, 127.6, 128.5, 128.6, 128.7, 129.1, 139.7, 139.9. Anal. Calcd for $C_{17}H_{18}OS_2$: C, 67.51; H, 6.00%. Found: C, 67.23; H, 6.00%.

(1*R,2*S**)-2-[(*S**)-phenyl(4-trifluoromethylphenyl)methyl]-1,3-dithiane 1-oxide (6b):** Mp 173–174 ºC (hexane/EtOAc); IR (Nujol) 2923, 2854, 1417, 1326, 1161, 1128, 1070, 1051, 735, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.78–1.84 (m, 1H), 2.45–2.64 (m, 3H), 2.86–2.91 (m, 1H), 3.15–3.19 (m, 1H), 4.31 (d, *J* = 12.0 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 7.25–7.29 (m, 1H), 7.32–7.37 (m, 4H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.2, 29.4, 46.7, 52.5, 65.0, 124.1 (q, *J* = 271 Hz), 126.2 (q, *J* = 3.8 Hz), 127.9, 128.6, 129.1 (merged signal), 130.0 (q, *J* = 32.0 Hz), 138.9, 144.0. HRMS (*m/z*) Calcd for $C_{18}H_{17}OF_3S_2$: 370.0673. Observed: 370.0672. Anal. Calcd for $C_{18}H_{17}OF_3S_2$: C, 58.36; H, 4.63%. Found: C, 58.15; H, 4.58%. X-Ray quality crystals were grown from acetonitrile/hexane. CCDC No.: 681750. Copies of the X-ray crystallographic data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: 44-1223-3360033 or E-mail: deposit@ccdc.cam.ac.uk.

(1*R,2*S**)-2-[(*S**)-1-phenylethyl]-1,3-dithiane 1-oxide (6c, the major isomer):** Mp 126–128 ºC (hexane/EtOAc); IR (Nujol) 2924, 2854, 1454, 1375, 1038 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45 (d, *J* = 7.0 Hz, 3H), 1.72–1.78 (m, 1H), 2.33 (ddd, *J* = 3.0, 13.5, 13.5 Hz, 1H), 2.50–2.61 (m, 1H), 2.66–2.70 (m, 1H), 2.83–2.90 (m, 1H), 3.01–3.06 (m, 1H), 3.13–3.19 (m, 1H), 3.80 (d, *J* = 5.5 Hz, 1H), 7.27–7.33 (m, 3H), 7.34–7.38 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.4, 19.3, 29.2, 41.5, 46.8, 68.5, 127.6, 128.1, 129.0, 142.5. Anal. Calcd for $C_{12}H_{16}OS_2$: C, 59.96; H, 6.71%. Found: C, 59.70; H, 6.62%.

2-benzyl-2-methyl-1,3-dithiane 1-oxide (10): Mp 126–128 ºC (hexane/EtOAc); IR (Nujol) 2923, 2853, 1456, 1374, 1071, 1006, 748, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.62 (s, 3H), 2.13–2.22 (m, 1H), 2.32–2.39 (m, 2H), 2.62–2.68 (m, 1H), 2.76 (ddd, *J* = 3.0, 13.5, 13.5 Hz, 1H), 3.07 (ddd, *J* = 4.0, 4.0, 13.5 Hz, 1H), 3.21 (s, 2H), 7.27–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 13.9, 25.0, 28.8, 43.4, 46.4, 62.4, 127.6, 128.2, 131.3, 133.8. Anal. Calcd for $C_{12}H_{16}OS_2$: C, 59.96; H, 6.71%. Found: C, 59.79; H, 6.42%.

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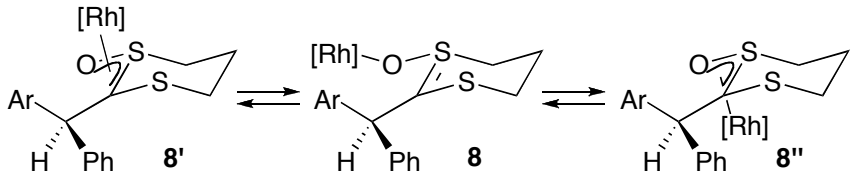

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