Substitution Reactions of 3-Sulfolenyl Dianions

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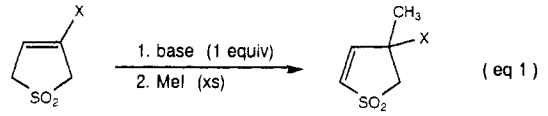
It has been well established that substituted 3-sulfolenes are stable precursors to the synthetically useful 1,3-butadienes.[1] The direct deprotonation/substitution reaction of a 3-sulfolene at the α-position is probably the most convenient method for the preparation of these masked dienes.[2] The preexisting substituent on an unsymmetrically substituted starting material has a strong directing effect on the regioselectivity of the deprotonation/substitution reaction. In general, when a 3-sulfolene bears at its 3-position a moderate carbanion stabilizing group, such as phenyl, phenylthio, or trimethylsilyl, the deprotonation/substitution reaction occurs exclusively at the 5-position. Whereas a nonstabilizing substituent, such as chloro, bromo, or alkyl, at the 3-position causes the reaction to occur exclusively at the 2-position.[3] In almost all of the known cases, only α- and α'-substitution products were obtained. Although γ-substitution reactions are also possible pathways for the sulfolenyl anion, they are rarely observed.[4]

However, when a 3-sulfolene which contains a strong electron-withdrawing group at its 3-position is treated with 1 equiv of base followed by a slight excess of an electrophile, γ-substitution becomes the major reaction. α-Substitution does not occur or takes place only to a little extent. For example, the reaction of 3-(methoxycarbonyl)-3-sulfolene **1a**[5] with 1 equiv of *n*-BuLi and an excess of MeI did not give the α-methylated product **3a** but gave 4-(methoxycarbonyl)-4-methyl-2-sulfolene **2a** as the only product (eq 1). 3-(Phenylsulfonyl)-3-sulfolene

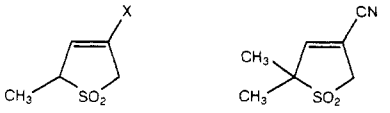


(eq 1)

1a. X= $-CO_2Me$ **2a**
1b. X= $-SO_2Ph$ **2b**
1c. X= $-CN$ **2c**

(**1b**)[6] and 3-cyano-3-sulfolene (**1c**)[7] behaved similarly under the conditions so that γ-substitutions took place to give the 2-sulfolenes **2b** and **2c**, respectively (Table I). In the case of **1c**, there is a competition between α- and γ-substitutions so that products **3c–5** were also observed. Although substituted 2-sulfolenes **2a–c** were obtained in good yields, they are not precursors for substituted 1,3-dienes and hence are not very synthetically useful. The attempted deprotonation/acetylation of **1a** yielded only the O-acetylated product **6** (entry **5**, Table I).

The preference of γ-substitution for **1a–c** under these conditions indicates that the negative charge density of the allylic anions **7a** and **7b** are higher at the γ-position than the α-position, while the negative charge density of **7c** is more or less evenly distributed between the α- and γ-positions.[8]



3a. X= $-CO_2Me$
3b. X= $-SO_2Ph$
3c. X= $-CN$

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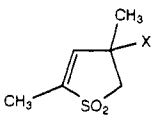

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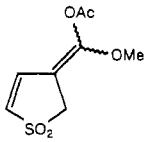

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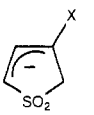
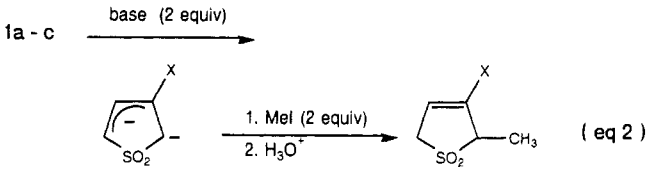


7a. X= $-CO_2Me$
7b. X= $-SO_2Ph$
7c. X= $-CN$

While the monocarbanion/substitution reactions failed to produce derivatives of **9a–c** effectively, the dianion strategy has been very successful toward this goal. With the use of 2 equiv of *n*-BuLi, compound **1a** was deprotonated twice at −78 °C to yield the α,α'-dianion **8a**. Substitution of this dianion with 1 equiv of MeI took place at the more reactive site to yield the 2-methylated product **9a** (eq 2). It was later found that at this low temperature



(eq 2)

8a. X= $-CO_2Me$ **9a**
8b. X= $-SO_2Ph$ **9b**
8c. X= $-CN$ **9c**

the carbanion on the 5-position was unreactive toward methylation. Thus, monomethylation of this dianion **8a** could be conveniently performed by treatment with an excess of MeI (≥2 equiv) followed by aqueous acid at −78 °C. No dimethylated product was observed so long as the reaction was kept below −78 °C before aqueous workup.

Since the spectral properties of the other possible regioisomer **3a** were expected very difficult to be distinguished from those of **9a**, we needed more evidences to unequivocally prove the structural assignment of **9a**. Thus, **9a** was treated with 1 equiv of *n*-BuLi followed by workup with MeI (eq 3). This reaction gave 42% yield of the

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Table I. Substitution Reactions of Monoanions of 3-Sulfolenes

reactant (1 equiv)	base (equiv)	E^+ (equiv)	products (yields,[a] %)
1a	*n*-BuLi (1)	MeI (2)	**2a** (67)
1b	*n*-BuLi (1)	MeI (2)	**2b** (71)
1c	LiHMDS (1)/HMPA	MeI (20)	**2c** (13) + **3c** (14) + **4** (3) + **5** (24)
1c	LiHMDS (0.5)/HMPA	MeI (20)	**2c** (35) + **3c** (36) + **5** (17)
1a	*n*-BuLi (1)	AcCl (1)	**6** (58)

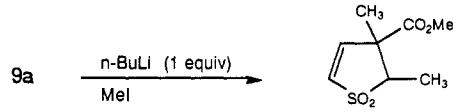
[a] The numbers in parentheses are isolated yields after column chromatography.

Table II. Substitution Reactions of Dianions of 3-Sulfolenes

reactant	equiv of *n*-BuLi	E^+ (equiv)	products (yields,[a] %)
1a	2	MeI (2)	**9a** (75)
1b	2	MeI (2)	**9b** (76)[b]
1c	2	MeI (2)	**9c** (75)
1a	2	AcCl (0.4)	**11** (72)[c]
1c	2	AcCl (0.4)	**12** (74)[c,d]
1c	2	PhCOCl (0.4)	**13** (72)[c]

[a] The numbers in parentheses are isolated yields unless otherwise noted. [b] Accompanied with 2-methyl-3-(phenylsulfonyl)-2,3-dihydrothiophene dioxide in 18% yield. [c] The yields are based on recovered starting materials. [d] We were unable to obtain product **12** free from the starting material, so the yield was estimated from the integrations of ^{1}H NMR peaks.

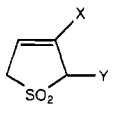
dimethylated 2-sulfolene **10**, which shows two vinylic protons in the ^{1}H NMR spectrum.



(eq 3)

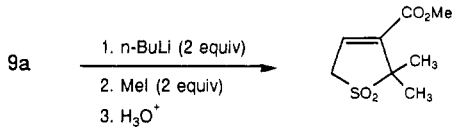
10

Compounds **1b** and **1c** could as well be doubly deprotonated with 2 equiv of *n*-BuLi at low temperatures giving the corresponding dianions **8b** and **8c**, respectively. Monosubstitution of dianions **8a–c** with different electrophiles, such as CH_3I and acyl chlorides, lead to the 2-substituted 3-sulfolenes (Table II). The control of the temperature is very essential for the success of the generation of the dianions **8a–c**. At slightly higher temperatures the yields are much lower due to the decomposition of the anionic species. During the course of acylation reactions, the acyl chlorides were used in insufficient quantity to avoid O-acylation of the primary products **11–13**. In these cases, starting materials could be recovered by chromatography.



11, X= – CO_2CH_3, Y=CH_3CO–
12, X= – CN, Y=CH_3CO–
13, X= – CN, Y=PhCO–

Although dianions **8a–c** are readily generated, many other 3-sulfolenes which do not have a strong electron-withdrawing substituent failed to yield their corresponding α,α'-dianions in our hands.[9] For example, 3-chloro-3-sulfolene and 3-methyl-3-sulfolene gave only monoanion in the presence of 2 equiv of *n*-BuLi at −105 °C, and they decomposed rapidly above −90 °C. Attempted generation of the dianion of 3-(phenylthio)-3-sulfolene and subsequent substitution were also unsuccessful. It is interesting to note that compound **9a** could be doubly deprotonated and monomethylated again to give the geminal dimethylated 3-sulfolene **14** (eq 4).



(eq 4)

14

The examples described herein illustrate that although some 3-sulfolenes such as **1a–c** fail to yield disubstituted 3-sulfolenes under monodeprotonation/substitution reaction conditions, their α,α'-dianions can be easily generated and the subsequent reactions with electrophiles can lead to synthetically useful di- and trisubstituted 3-sulfolenes.

Experimental Section

General. NMR spectra were determined as solutions in $CDCl_3$ on a Bruker AW-80 or a Bruker MSL-200 spectrometer. IR spectra were determined on a Perkin-Elmer 882 IR spectrophotometer. Mass spectra and high-resolution mass spectra were determined on a VG-70-250S mass spectrometer. Elemental analyses were taken on a Perkin-Elmer 240C analyzer. Melting points were determined on a Yamado MP-21 apparatus. All solvents were freshly distilled before use. 3-(Methoxycarbonyl)-3-sulfolene (**1a**) was purchased from Fluka and used without further purification. 3-(Phenylsulfonyl)-3-sulfolene (**1b**)[6,10] and 3-cyano-3-sulfolene[7] (**1c**) were prepared according to literature procedures. The HPLC column used was a LiChrosorb column from Merck.

3-(Methoxycarbonyl)-3-methyl-2,3-dihydrothiophene 1,1-Dioxide (2a). To a stirred solution of 3-(methoxycarbonyl)-2,5-dihydrothiophene 1,1-dioxide (**1a**) (0.1174 g, 0.67 mmol) in THF (10 mL) was added *n*-BuLi (0.45 mL, 1.5 M, 0.68 mmol) in cyclohexane dropwise at −78 °C, and the mixture was kept stirring for 30 min at the same temperature. CH_3I (0.09 mL, 1.34 mmol) was added, and the stirring was continued for 2 h before the solution was allowed to warm to room temperature. After another 2 h, the reaction was quenched with saturated NH_4Cl, extracted into EtOAc, dried ($MgSO_4$), and concentrated. The yellow oil was purified by HPLC (EtOAc/hexane, 1:1) to afford **2a** (0.0849 g, 67%) as a yellow oil: ^{1}H NMR (80 MHz) δ 1.59 (3 H, s), 3.10 (1 H, d, J = 13.2 Hz), 3.84 (1 H, d, J = 13.2 Hz), 3.77 (3 H, s), 6.57 (1 H, d, J = 6.4 Hz), 6.75 (1 H, d, J = 6.4 Hz); IR (neat) 1736, 1604, 1300, 1146, 1100 cm^{-1}; MS m/z 191 (M^+ + 1), 115 (100). Anal. Calcd for $C_7H_{10}O_4S$: C, 44.20; H, 5.30. Found: C, 44.33; H, 4.81.

3-Methyl-3-(phenylsulfonyl)-2,3-dihydrothiophene 1,1-Dioxide (2b). To a stirred solution of 3-(phenylsulfonyl)-2,5-dihydrothiophene 1,1-dioxide (**1b**) (0.0920 g, 0.35 mmol) in THF (10 mL) was added *n*-BuLi (0.2 mL, 1.75 M, 0.35 mmol) in cyclohexane dropwise at −78 °C, and the mixture was kept stirring for 30 min at the same temperature. CH_3I (0.045 ml, 0.71 mmol) was added, and stirring was continued for another 1 h before the solution was allowed to warm to room temperature. The reaction was then quenched with saturated NH_4Cl, extracted into EtOAc, dried ($MgSO_4$), and concentrated. The yellow solid was purified by HPLC (EtOAc/hexane, 1:1) to afford **2b** (0.0693 g, 71%) as white crystals: mp 142.5–143.5 °C; ^{1}H NMR (80 MHz) δ 1.76 (3 H, s), 3.16 (1 H, d, J = 14.0 Hz), 3.79 (1 H, d, J = 14.0 Hz), 6.75 (2 H, s), 7.59–7.88 (5 H, m); IR (KBr) 1442, 1298, 1140, 1075 cm^{-1}; MS m/z 272 (M^+), 131 (100), 83, 78, 77, 41. Anal. Calcd for $C_{11}H_{12}O_4S_2$: C, 48.51; H, 4.44. Found: C, 48.57; H, 4.30.

Methylation of the Monoanion of 3-Cyano-2,5-dihydrothiophene 1,1-Dioxide (1c). To a solution containing 3-cyano-2,5-dihydrothiophene 1,1-dioxide (**1c**) (0.2080 g, 1.45 mmol), CH_3I (1.82 mL, 29.1 mmol), and HMPA (2.02 mL, 11.6 mmol) in THF (20 mL) at −105 °C was added LiHMDS [prepared from

(9) Tao, Y. T.; Chen, M. L. *J. Org. Chem.* **1988**, *53*, 69.

(10) Compound **9b** has been prepared by an alternative route: Chou, S. S. P.; Tsai, C. Y.; Sun, C. M. *J. Chin. Chem. Soc.* **1989**, *36*, 149.

HMDS (0.37 mL, 1.74 mmol) and *n*-BuLi (0.86 mL, 1.69 M, 1.45 mmol)]. The mixture was warmed to 30 °C and stirred for 4 h. The reaction was then quenched with saturated NH_4Cl, extracted into EtOAc, dried ($MgSO_4$), and concentrated. The yellow oil was purified by HPLC (EtOAc/hexane, 1:1) to afford **2c** (0.0287 g, 13%), **3c** (0.0311 g, 14%), **4** (0.0066 g, 3%), and **5** (0.0603 g, 24%).

3-Cyano-3-methyl-2,3-dihydrothiophene 1,1-dioxide (2c): colorless oil; ^1H NMR (200 MHz) δ 1.79 (3 H, s), 3.30 (1 H, d, J = 13.7Hz), 3.71 (1 H, d, J = 13.7 Hz), 6.68 (1 H, d, J = 6.6 Hz), 6.84 (1 H, d, J = 6.6 Hz); IR (neat) 2244, 1603, 1312, 1306, 1158, 1126 cm^{-1}; MS m/z 157 (M^+), 128, 66, 41(100); HRMS calcd for $C_6H_7NO_2S$ 157.0198, found 157.0188. The purity of **2c** was judged to be ≥90% by ^1H NMR spectral determinations.

4-Cyano-2-methyl-2,5-dihydrothiophene 1,1-dioxide (3c): white crystals; mp 92–93 °C; ^1H NMR (200 MHz) δ 1.52 (3 H, d, J = 7.2 Hz), 3.90–3.94 (2 H, m), 3.94–4.07 (1 H, m), 6.79–6.82 (1 H, m); IR (KBr) 2227, 1314, 1243, 1129 cm^{-1}; MS m/z 93 (M^+ – 64, 100), 66; HRMS calcd for $C_6H_7NO_2S$ 157.0198, found 157.0206. The purity of **3c** was judged to be ≥90% by ^1H NMR spectral determinations.

4-Cyano-2,2-dimethyl-2,5-dihydrothiophene 1,1-dioxide (4): pale yellow crystals; mp 76–77 °C; ^1H NMR (200 MHz) δ 1.54 (6 H, s), 3.91 (2 H, d, J = 1.9 Hz), 6.78 (1 H, t, J = 1.9 Hz); IR (KBr) 2247, 1299, 1118 cm^{-1}; MS m/z 107 (M^+ – 64, 100), 80. Anal. Calcd for $C_7H_9NO_2S$: C, 49.10; H, 5.30; N, 8.18. Found: C, 48.95; H, 5.21; N, 8.05.

3-Cyano-3,5-dimethyl-2,3-dihydrothiophene 1,1-dioxide (5): white crystals; mp 60–61 °C; ^1H NMR (200 MHz) δ 1.74 (3 H, s), 2.11 (3 H, d, J = 1.6 Hz), 3.28 (1 H, d, J = 13.7 Hz), 3.72 (1 H, d, J = 13.7 Hz), 6.20 (1 H, q, J = 1.6 Hz); IR (KBr) 2237, 1304, 1153, 1114 cm^{-1}; MS m/z 171 (M^+), 106, 92, 79 (100). Anal. Calcd for $C_7H_9NO_2S$: C, 49.10; H, 5.30; N, 8.18. Found: C, 48.71; H, 5.32; N, 8.34.

By the same procedure from **1c** and MeI using 0.5 equiv of LiHMDS/HMPA, the reaction afforded a mixture of **2c** (35%), **3c** (36%), and **5** (17%).

3-(Acetoxymethoxymethylene)-2,3-dihydrothiophene 1,1-Dioxide (6). To a stirred solution of **1a** (0.1174 g, 0.67 mmol) in THF (10 mL) was added *n*-BuLi (0.45 mL, 1.5 M, 0.68 mmol) in cyclohexane dropwise at –78 °C, and the mixture was stirred for 30 min at the same temperature. AcCl (91 mg, 1.34 mmol) was added, and the stirring was continued for 2 h before the solution was allowed to warm to room temperature. After another 2 h, the reaction was quenched with saturated NH_4Cl and extracted into EtOAc, dried ($MgSO_4$), and concentrated. The crude oil was purified by HPLC (EtOAc/hexane, 1:1) to afford **6** (0.1461 g, 58%) as a colorless oil: ^1H NMR (80 MHz) δ 2.32 (3 H, s), 3.75 (2 H, s), 3.85 (3 H, s), 6.76 (1 H, d, J = 5.2 Hz), 6.97 (1 H, d, J = 5.2 Hz); IR (neat) 1740, 1600, 1300, 1130 cm^{-1}; MS m/z 218 (M^+), 187, 176, 145, 112, 111, 97, 83, 82, 81, 69, 68, 59, 51, 43 (100). Anal. Calcd for $C_8H_{10}O_5S$: C, 44.03; H, 4.62. Found: C, 44.16; H, 4.71.

3-(Methoxycarbonyl)-2-methyl-2,5-dihydrothiophene 1,1-Dioxide (9a). To a stirred solution of **1a** (0.3070 g, 1.74 mmol) in THF (20 mL) was added *n*-BuLi (2.06 mL, 1.69 M, 3.49 mmol) in cyclohexane dropwise at –78 °C, and the mixture was kept stirring for 30 min at the same temperature. CH_3I (0.22 mL, 3.49 mmol) was added, and stirring was continued for 5 min at –78 °C. The reaction was then quenched with saturated NH_4Cl, extracted into EtOAc, dried ($MgSO_4$), and concentrated. The yellow oil was purified with a silica gel column (EtOAc/hexane, 1:2) to give **9a** (0.2491 g, 75%) as a light yellow oil: ^1H NMR (200 MHz) δ 1.53 (3 H, d, J = 7.2 Hz), 3.84 (3 H, br s) 3.94 (2 H, br s), 3.99 (1 H, q, J = 7.2 Hz), 7.02 (1 H, br s); IR (neat) 1728, 1320, 1135, 1080 cm^{-1}; MS m/z 126 (M^+ – 64, 100), 111. Anal. Calcd for $C_7H_{10}O_4S$: C, 44.20; H, 5.30. Found: 44.43; H, 5.05.

2-Methyl-3-(phenylsulfonyl)-2,5-dihydrothiophene 1,1-Dioxide (9b) and 2-Methyl-3-(phenylsulfonyl)-2,3-dihydrothiophene 1,1-Dioxide. To a stirred solution of **1b** (0.1355 g, 0.525 mmol) in THF (10 mL) was added *n*-BuLi (0.62 mL, 1.69 M, 1.05 mmol) in cyclohexane dropwise at –78 °C, and the mixture was kept stirring for 30 min at the same temperature. CH_3I (0.07 mL, 1.05 mmol) was added, and stirring was continued for another 10 min at –78 °C. The reaction was then quenched with saturated NH_4Cl, extracted into EtOAc, dried ($MgSO_4$), and concentrated. The yellow oil was purified by flash column chromatography (EtOAc/hexane, 1:2) to afford **9b** and its isomer 2-methyl-3-(phenylsulfonyl)-2,3-dihydrothiophene 1,1-dioxide (7:2) (0.1347 g, 94%) as a yellow oil. The spectral data of compounds **9b** and its isomer are identical with those reported in literature.[10]

3-Cyano-2-methyl-2,5-dihydrothiophene 1,1-Dioxide (9c). To a stirred solution of **1c** (0.1217 g, 0.85 mmol) in THF (10 mL) was added *n*-BuLi (1.01 mL, 1.69 M, 1.7 mmol) in cyclohexane dropwise at –105 °C, and the temperature was raised gradually to –90 °C. CH_3I (0.11 mL, 1.7 mmol) was added, and the reaction mixture was allowed to warm to –78 °C. The reaction was quenched with saturated NH_4Cl, extracted into EtOAc, dried ($MgSO_4$), and concentrated. The yellow solid was purified with a silica gel column (EtOAc/hexane, 1:2) to give **9c** (0.0999 g, 75%) as white crystals: 96–97 °C dec; ^1H NMR (200 MHz) δ 1.60 (3 H, d, J = 6.0 Hz), 3.83–4.00 (3 H, m), 6.80–6.96 (1 H, m); IR (KBr) 2231, 1605, 1314, 1307, 1130 cm^{-1}; MS m/z 107 (M^+ – 50), 93 (100), 66. Anal. Calcd for $C_6H_7NO_2S$: C, 45.84; H, 4.49; N, 8.91. Found: C, 45.99; H, 4.63; N, 8.98.

3-(Methoxycarbonyl)-2,3-dimethyl-2,3-dihydrothiophene 1,1-Dioxide (10). To a stirred solution of **9a** (0.1395 g, 0.73 mmol) in THF (10 mL) was added *n*-BuLi (0.49 mL, 1.5 M, 0.73 mmol) in cyclohexane dropwise at –78 °C, and the mixture was stirred for 20 min at the same temperature. CH_3I (0.09 mL, 1.46 mmol) was added, and the mixture was allowed to warm to room temperature and stirred for another 2 h. The reaction was then quenched with saturated NH_4Cl, extracted into EtOAc, dried ($MgSO_4$), and concentrated. The yellow oil was purified by HPLC (EtOAc/hexane, 1:1) to afford **10** (0.0624 g, 42%) as a colorless oil: ^1H NMR (80 MHz) δ 1.30 (3 H, d, J = 6.4 Hz), 1.56 (3 H, s), 3.10 (1 H, q, J = 6.4 Hz), 3.74 (3 H, s), 6.65 (2 H, s); IR (neat) 1730, 1318, 1299, 1132 cm^{-1}; MS m/z 204 (M^+), 145, 129, 59, 41 (100); HRMS calcd for $C_8H_{12}O_4S$ 204.0456, found 204.0449. Anal. Calcd for $C_8H_{12}O_4S$: C, 47.04; H, 5.92. Found: C, 47.22; H, 6.11.

2-Acetyl-3-(methoxycarbonyl)-2,5-dihydrothiophene 1,1-Dioxide (11). To a stirred solution of **1a** (0.1906 g, 1.08 mmol) in THF (20 mL) was added *n*-BuLi (1.28 mL, 1.69 M, 2.17 mmol) in cyclohexane dropwise at –78 °C, and the mixture was stirred for another 5 min at –78 °C. Acetyl chloride (0.031 mL, 0.43 mmol) in THF was added, and the stirring was kept for another 5 min whereupon 5% HCl in THF was added and the reaction mixture was allowed to warm to room temperature. Brine was added, and the reaction mixture was extracted with EtOAc, dried ($MgSO_4$), and concentrated. The yellow oil was purified by HPLC (EtOAc/hexane, 1:1) to afford **11** (0.0683 g, 72%) as a colorless oil: ^1H NMR (200 MHz) δ 2.49 (3 H, s), 3.80 (3 H, s), 3.92–4.13 (2 H, m), 4.99 (1 H, br s), 7.18–7.21 (1 H, m); IR (neat) 1720, 1360, 1325, 1160, 1120 cm^{-1}; MS m/z 218 (M^+) 176, 139, 43 (100). Anal. Calcd for $C_8H_{10}O_5S$: C, 44.03; H, 4.62. Found: C, 44.19; H, 4.78.

2-Acetyl-3-cyano-2,5-dihydrothiophene 1,1-Dioxide (12). To a stirred solution of **1c** (0.1925 g, 1.35 mmol) in THF (20 mL) was added *n*-BuLi (1.59 ml, 1.69M, 2.69 mmol) in cyclohexane dropwise at –105 °C, and the mixture was stirred for another 5 min at –105 °C. Acetyl chloride (0.038 mL, 0.538 mmol) in THF was added, and the stirring was continued for another 5 min whereupon 5% HCl in THF was added and the reaction mixture was allowed to warm to room temperature. Brine was added, and the reaction mixture was extracted with EtOAc, dried ($MgSO_4$), and concentrated. The yellow solid could not be further purified by chromatography. From the ^1H NMR spectrum, the estimated ratio of **1c** and **12** was 69:31. The yield of **12** based on recovered starting material was 0.0738 g (74%): ^1H NMR (200 MHz) δ 2.52 (3 H, s), 3.92–4.02 (2 H, m), 4.84 (1 H, br s), 7.03–7.10 (1 H, m).

2-Benzoyl-3-cyano-2,5-dihydrothiophene 1,1-Dioxide (13). To a stirred solution of **1c** (0.2446 g, 1.71 mmol) in THF (20 mL) was added *n*-BuLi (2.02 mL, 1.69 M, 3.42 mmol) in cyclohexane dropwise at –105 °C, and the mixture was stirred for another 5 min at –105 °C. Benzoyl chloride (0.079 mL, 0.684 mmol) in THF was added, and the stirring was continued for 5 min whereupon 5% HCl in THF was added and the reaction mixture was allowed to warm to room temperature. Brine was added, and the reaction mixture was extracted with EtOAc, dried ($MgSO_4$), and concentrated. The yellow solid was purified by flash column chromatography (EtOAc/hexane, 1:1) to afford 0.2649 g of a mixture of compound **1c** and **13** in 2:1 ratio. Based on the recovered starting material, compound **13** was produced in 0.1226 g (72%). The

mixture was purified by HPLC (EtOAc/hexane, 1:1) to give **13** (28%) as pale yellow crystals: mp 131–132 °C dec; ^{1}H NMR (200 MHz) δ 4.00–4.12 (2 H, m), 5.67–5.70 (1 H, m), 7.11–7.15 (1 H, m), 7.53–7.88 (3 H, m), 8.02–8.08 (2 H, m); IR (KBr) 2231, 1678, 1327, 1282, 1145 cm^{-1}; MS m/z 247 (M^+), 183, 105 (100), 77; HRMS calcd for $C_{12}H_9NO_3S$ 247.0303, found 247.0306. The purity of **13** was judged to be ≥90% by ^{1}H NMR spectral determinations.

3-(Methoxycarbonyl)-2,2-dimethyl-2,5-dihydrothiophene 1,1-Dioxide (14). To a stirred solution of **9a** (0.2701 g, 1.42 mmol) in THF (30 mL) was added *n*-BuLi (1.68 mL, 1.69 M, 2.84 mmol) in cyclohexane dropwise at −105 °C, and the temperature was raised gradually to −90 °C. CH_3I (0.18 ml, 2.84 mmol) was added, and the reaction was slowly warmed to −78 °C. The reaction was quenched with saturated NH_4Cl, extracted into EtOAc, dried ($MgSO_4$), and concentrated. The yellow oil was purified with a silica gel column (EtOAc/hexane, 1:2) to give **14** (0.2685 g, 92%) as white crystals: mp 77–78 °C dec: ^{1}H NMR (200 MHz) δ 1.61 (6 H, s), 3.82 (3 H, s), 3.86 (2 H, d, J = 3.3 Hz), 7.00 (1 H, t, J = 3.3 Hz); IR (KBr) 1708, 1431, 1329, 1291, 1161, 1115 cm^{-1}; MS m/z 173 (M^+ − 31), 140 (100), 108. Anal. Calcd for $C_8H_{12}O_4S$: C, 47.04; H, 5.92. Found: C, 47.06; H, 6.15.

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Registry No. **1a**, 67488-50-0; **1b**, 108919-91-1; **1c**, 122131-77-5; **2a**, 104664-92-8; **2b**, 127844-17-1; **2c**, 128114-75-0; **3c**, 128114-76-1; **4**, 128114-77-2; **5**, 128114-78-3; **6**, 128114-79-4; **9a**, 128114-80-7; **9b**, 123559-84-2; **9c**, 128114-81-8; **10**, 128114-82-9; **11**, 128114-83-0; **12**, 128114-84-1; **13**, 128114-85-2; **14**, 128114-86-3; 2-methyl-3-(phenylsulfonyl)-2,3-dihydrothiophene 1,1-dioxide, 123559-85-3.

Supplementary Material Available: ^{1}H NMR spectra for compounds **2c**, **3c**, and **13** (3 pages). Ordering information is given on any current masthead page.

Triphenylsilane: A Useful Radical-Based Reducing Agent[1]

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It has been shown that tris(trimethylsilyl)silane is effective in reducing organic halides by a free-radical mechanism whereas simple trialkylsilanes are far less efficient.[3,4] This discovery followed from measurements of silicon–hydrogen bond dissociation enthalpies[5] since D{$(Me_3Si)_3Si$–H} = 79 kcal mol^{-1} as opposed to D(Et_3Si–H) = 91 kcal mol^{-1}. This implies that the crucial chain carrying step in the reduction, i.e. hydrogen abstraction by simple alkyl radicals from tris(trimethylsilyl)silane, is exothermic by roughly 19 kcal mol^{-1} whereas for trialkylsilanes the corresponding figure is only about 7 kcal mol^{-1}.

In the course of our investigations on the effects of other substituents on D(Si–H), we have found that phenyl groups also induce a weakening of the silicon–hydrogen bond.[6] Although the effect is not as dramatic as for the silyl moieties, D(Si–H) in triphenylsilane is about 7 kcal mol^{-1} lower than D(Et_3Si–H),[6,7] suggesting that Ph_3SiH would also be a useful reducing agent at moderate temperatures. Results for the kinetics of reduction of bromohexadecane by several phenyl-substituted silanes are now reported and confirm that suggestion.

Experimental Section

Triphenylsilane, diphenylmethylsilane, phenyldimethylsilane, and the remaining materials used in the experiments were commercially available.

In a typical experiment, 11 mg of dibenzoyl peroxide (0.0087 M) were added to 5 mL of a heptane solution of Ph_3SiH (0.067 M), bromohexadecane (0.052 M), and undecane (internal standard; 100 μL). The mixture was kept at 90 ± 2 °C, and the reaction was followed quantitatively by gas chromatography (Hewlett-Packard 5890) over a period of about 5 h and to >80% conversion of the bromide. Products were identified by GC/mass spectrometry (Hewlett-Packard 5970A). Both instruments were equipped with cross-linked methylsilicon columns, and authentic samples of reagents and products were used for calibration. The same procedure was used in the competition experiments involving Ph_3SiH and the other silanes. However, the low reactivity of Ph_2MeSiH and $PhMe_2SiH$ required an increase of dibenzoyl peroxide concentration to ca. 0.025 M in the case of Ph_2MeSiH and 0.03 M for $PhMe_2SiH$. The relative concentrations of each pair of silanes were adjusted so as to optimize the experimental conditions, e.g. [Ph_3SiH]:[Ph_2MeSiH] = 1:3 and [Ph_3SiH]:[$PhMe_2SiH$] = 1:4.

Results and Discussion

A kinetic description of the radical chain mechanism reactions 1–5 was formulated by applying the steady-state approximation to [R′•] and by assuming that the consumption of silane in reaction 2 was negligible. Since halogen abstraction by silyl radicals is extremely rapid,[8,9] reaction 4 must represent the rate determining propagation step. The result is given in eq 6. Plots of ln ([R_3SiH]/[R_3SiH]$_0$) versus $e^{-k_1t/2}$ (Figure 1) led to values for $2k_4^2/k_1k_5$. For triphenylsilane (R = Ph), we found k_4 = (3.0 ± 0.3) × 10^4 M^{-1} s^{-1} at 90 °C in heptane by applying literature data[10,11] for k_1 (5.9 × 10^{-5} s^{-1}) and k_5 (1.3 × 10^{10} M^{-1} s^{-1}).

$$(PhCO)_2 \xrightarrow{k_1} PhCO_2^{\bullet} \rightarrow Ph^{\bullet} + CO_2 \quad (1)$$

$$PhCO_2^{\bullet}/Ph^{\bullet} + R_3SiH \xrightarrow{k_2} R_3Si^{\bullet} + PhCO_2H/PhH \quad (2)$$

$$R_3Si^{\bullet} + R'Br \xrightarrow{k_3} R'^{\bullet} + R_3SiBr \quad (3)$$

$$R'^{\bullet} + R_3SiH \xrightarrow{k_4} R_3Si^{\bullet} + R'H \quad (4)$$

$$R'^{\bullet} + R'^{\bullet} \xrightarrow{k_5} R'R \quad (5)$$

$$\ln([R_3SiH]_o/[R_3SiH]_0) = \{2k_4^2[(PhCO_2)_2]_0/k_1k_5\}(e^{-k_1t/2} - 1) \quad (6)$$

The error quoted for k_4 does not include uncertainties associated with k_1 and k_5. However, its order of magnitude confirms the thermochemically based suggestion that Ph_3SiH is a useful reducing agent.[12] Moreover, the value

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