One-Pot Synthesis of 4,5-Unsubstituted 1,3-Dithioles and 2-Alkylidene-1,3-dithioles from 1,3-Dithiolane *S*-Oxides

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Dedicated to Prof. Dr. Hansjörg Sinn on the occasion of his 60th birthday.

An efficient synthesis of the title compounds via formal dehydration of the corresponding 1,3-dithiolane *S*-oxides with iodotrimethylsilane and diisopropylethylamine (Hünig's base) is reported.

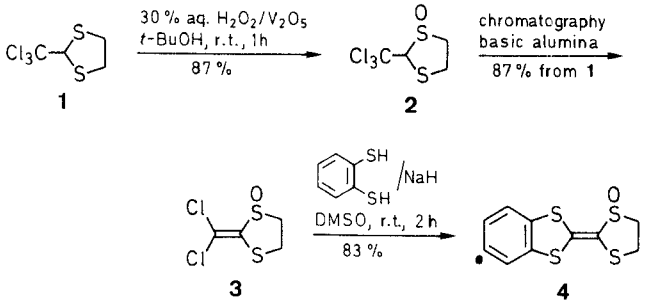
2-Alkylidene-1,3-dithioles (dithiafulvenes) are of particular interest as components of "organic metals"; tetrathiafulvalene being the most prominent example.[1] Consequently, synthesis of this special type of ketene thioacetal has been intensely studied.[2-4] However, in spite of the increasing importance of representatives with reduced symmetry,[3,4] only a limited range of routes, usually employing multistep procedures, is available for 4,5-unsubstituted derivatives. Thus, the ring C=C double bond has been introduced by dehydration of 4-hydroxy derivatives,[5] the exocyclic C=C moiety has been elaborated from 1,3-dithiole-2-thione[6] or 1,3-dithiolium salts,[7] and the C–S bonds have been formed by nucleophilic attack of alkene 1,1-dithiolates on haloalkenes.[8]

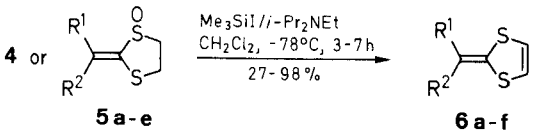
Our approach is based on the dehydration of 2-alkylidene-1,3-dithiolane *S*-oxides **5** which are usually readily available by peracid oxidation of the corresponding ketene thioacetals.[9,10] However, precursor **4** with only one of four sulfur atoms being part of a sulfoxide group requires an indirect approach involving a sequence of oxidation of **1**, dehydrochlorination of *S*-oxide **2**, and replacement of the halogen in **3** by benzene-1,2-dithiol.

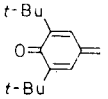
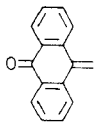
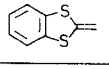
When *S*-oxides **4** or **5** are treated with iodotrimethylsilane in the presence of diisopropylethylamine (Hünig base) dithioles **6** are formed in a clean reaction. Probably, the reaction is initiated by *O*-silylation and followed by base-induced elimination of trimethylsilanol;[11] the liberated silanol consumes a second equivalent of the silylating agent which, therefore, has to be employed in twofold excess. However, with the substrates under study, the alternate route – [3 + 2]cycloreversion of the intermediate sulfur ylide giving thioketenes[12] – is not observed. Obviously, a zwitterionic resonance structure of **6**, where the positive charge is stabilized in an aromatic dithiolium system and the negative charge by the acceptor groups on the alkylidene moiety,[5] provides a strong driving-force for formation of the dithiole system.

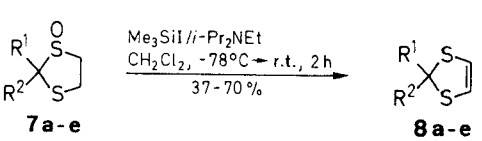
While dithioles **6a–e** are relatively stable compounds, tetrathiafulvalene derivative **6f** is sensitive to air oxidation during workup and is obtained only in moderate yield (Table). Compound **6f** is a known component of organic metals.[3]

The present approach can also be applied to 1,3-dithiolane *S*-oxides lacking the 2-alkylidene moiety. Thus, by the method given above, *S*-oxides **7a–e** are converted into dithioles **8a–e**. However, here a procedure avoiding a twofold excess of base at 20 °C allows conversion of **7a–e** into the corresponding thiocarbonyl compounds.[12]





	R^1	R^2		$R^1(R^2)C=$
5,6a	Ph	Ph	**5,6d**	
5,6b	Ph	NC–	**5,6e**	
5,6c	Ph	CH_3CH_2CO	**6f**	



7, 8	R^1	R^2
a	t-C_4H_9	H
b	CH_3	CH_3
c	$-(CH_2)_5-$	
d	Ph	CH_3
e	Ph	Ph

Dithiolane **1**[13] and dithiolane *S*-oxides **5a–e**,[10] **7a**,[14] **b,c**,[15] **d**,[16] **e**[17] were prepared by reported procedures.

Table. Dithiolanes **2**, **3** and Dithioles **6**, **8** Prepared

Product	Yield (%)	mp (°C)	Molecular Formula[a]	IR (neat or KBr) ν (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS) δ, J (Hz)	^{13}C-NMR ($CDCl_3$/TMS) δ
2	87	75	$C_4H_5Cl_3OS_2$ (239.6)	1060, 1040 (S=O), 790, 740 (C–Cl)	2.63–4.63 (m, 4H, CH_2), 5.20 (s, 1H, CH)	
3	87	70	$C_4H_4Cl_2OS_2$ (203.1)	1550 (C=C), 1040 (S=O), 970 (C–Cl)	2.5–3.2 (m, 1H, SOCH), 3.2–3.89 (m, 2H, SCH_2), 3.89–4.5 (m, 1H, SOCH)	
4	83	155–158	$C_{10}H_8OS_4$ (272.4)	1560, 1520 (C=C), 1030 (S=O)	2.7–3.16 (m, 1H, SOCH), 3.45–3.80 (m, 2H, SCH_2), 4.02–4.46 (m, 1H, SOCH), 7.05–7.40 (m, $4H_{arom}$)	
6a	92	103	$C_{16}H_{12}S_2$ (268.4)	3060 (CH)	6.17 (s, 2H, SCH), 7.2–7.45 (m, $10H_{arom}$)	117.3 (SCH), 124.9 (S_2C), 126.9–136.3 (C_{arom}), 142.5 (CPh_2)
6b	83	62.5	$C_{11}H_7NS_2$ (217.3)	2200 (CN), 1590, 1570, 1540, 1500 (C=C)	6.50, 6.69 (AB, 2H, J = 6.6), 7.1–7.8 (m, $5H_{arom}$)	93.0 (CN), 118.9, 126.1, 127.6, 128.8 (C_{arom}), 119.3, 120.0 (SCH), 134.2 (CS_2), 159.9 (PhC=)
6c	78	40	$C_{13}H_{12}OS_2$ (248.4)	1675, 1645	1.02 (t, 3H, CH_3, J = 7.1), 2.27 (q, 2H, CH_2, J = 7.1), 6.62 and 6.83 (d, 2H, SCH, J = 6.0), 7.1–7.62 (m, $5H_{arom}$)	8.6 (CH_3), 32.2 (CH_2), 118.0, 121.9, 124.3, 128.1 (C_{arom}), 129.6, 129.7 (SCH), 139.6 (CS_2), 163.0 (PhC=), 193.0 (C=O)
6d	96	192–195	$C_{17}H_{22}OS_2$ (306.5)	1610 (C=O), 1570, 1530	1.32 (s, 18H, CH_3), 6.76 (s, 2H, SCH), 7.05 (s, $2H_{quin}$)	29.5 (CH_3), 35.2 (CCH_3), 117.9, 126.5 (C_{quin}), 121.8 (SCH), 144.5 (CS_2), 160.3 (C_{quin}=), 184.8 (C=O)
6e	98	206	$C_{17}H_{10}OS_2$ (294.4)	1640 (C=O), 1590 (C=C)	6.45 (s, 2H, SCH), 7.2–8.4 (m, $8H_{arom}$)	117.9 (SCH), 126.0, 126.4, 127.0, 130.6, 131.7, 145.9 (C_{arom}), 139.3 (CS_2), 160.2 (C=CS_2), 183.8 (C=O)
6f	27	141[b]	$C_{10}H_6S_4$ (254.4)	1660 (C=C)	6.29 (s, 2H, SCH), 7.0–7.3 (m, $4H_{arom}$)	118.9 (SCH), 122.7, 125.7 (CH_{arom}), 121.9, 126.0, 137.0 (C_{arom}, C=C)
8a	64	oil	$C_7H_{12}S_2$ (160.3)	1585 (C=C)	0.97 (s, 9H, $C(CH_3)_3$, 4.89 (s, 1H, H-2), 5.97 (s, 2H, H-4, H-5)	25.2 ($C(CH_3)_3$), 38.0 ($C(CH_3)_3$), 67.5 (C-2), 116.9 (C=C)
8b	37	oil	$C_5H_8S_2$ (132.2)	1592 (C=C)	1.70 (s, 6H, CH_3), 5.97 (s, 2H, H-4, H-5)	31.4 (CH_3), 66.8 (C-2), 117.3 (C=C)
8c	70	oil	$C_8H_{12}S_2$ (172.3)	1598, 1596 (C=C)	1.43 (m, 2H, CH_2), 1.62 (m, 4H, CH_2), 2.15 (t, 4H, CH_2), 6.01 (s, 2H, H-4, H-5)	24.3, 25.0, 40.5 (CH_2), 73.3 (C-2), 116.8 (C=C)
8d	41	oil	$C_{10}H_{10}S_2$ (194.3)	1590 (C=C)	2.21 (s, 3H, CH_3), 6.04 (s, 2H, H-4, H-5), 7.25–7.4, 7.75 (m, $5H_{arom}$)	32.5 (CH_3), 72.2 (C-2), 116.6 (C=C), 126.8, 127.8, 128.2, 142.6 (C_{arom})
8e	39	60	$C_{15}H_{12}S_2$ (256.4)	1585 (C=C)	6.05 (s, 2H, H-4, H-5), 7.0–7.6 (m, $10H_{arom}$)	79.5 (C-2), 117.2 (C=C), 127.6–143.7 (C_{arom})

[a] Satisfactory microanalyses obtained: C ±0.38, H ±0.25, S ±0.21; for **6b** exact mass ($C_{11}H_7NS_2$): calc. 217.0020, found 216.9993; for **6f** exact mass ($C_{10}H_6S_4$): calc. 253.93523, found 253.9328; for **8b** exact mass ($C_5H_8S_2$): calc. 132.0067, found 132.0064.
[b] Ref. 3.

2-(Trichloromethyl)-1,3-dithiolane *S*-Oxide (2) and 2-(Dichloromethylene)-1,3-dithiolane *S*-Oxide (3):
30% aq Hydrogen peroxide (0.65 mL, 6.35 mmol) in *t*-BuOH (4 mL) is added dropwise to a stirred solution of dithiolane **1**[13] (1.42 g, 6.35 mmol) and V_2O_5 (58 mg, 0.3 mmol) in *t*-BuOH (13 mL) at 20 °C (water bath). The mixture is stirred for 1 h and the solvent removed under reduced pressure. The residue is chromatographed on a silica gel column (42 cm × 4 cm) using CH_2Cl_2, then *t*-BuOMe, and finally *t*-BuOMe/acetone (1:1) as eluents to afford compound **2** (Table).

Using the same procedure, but employing basic alumina [eluent $CHCl_3$/petroleum ether (1:1), then *t*-BuOMe/petroleum ether (1:1)] instead of silica gel in the chromatographie purification leads directly to dithiolane **3** (Table).

2-(1,3-Benzothiol-2-ylidene)-1,3-dithiolane *S*-Oxide (4):
Sodium hydride (1.07 g of a 90% suspension in mineral oil, 40 mmol) is suspended in DMSO (30 mL) and benzene-1,2-dithiol (2.5 g, 17.83 mmol) in DMSO (30 mL) is added dropwise with vigorous stirring, while the temperature is kept at 20 °C by immersion in a water bath. After hydrogen evolution has ceased (15 min), a solution of **3** (3.63 g, 17.83 mmol) in DMSO (20 mL) is added. The reaction mixture is stirred for 2 h at r.t. and poured into ice/water (250 mL). The precipitate is collected by filtration and washed with petroleum ether bp 60–70 °C. Product **4** is purified by recrystallization from $CHCl_3$/EtOH or $CHCl_3$/toluene (Table).

2-Alkylidene-1,3-dithioles 6; General Procedure:
At −78 °C under nitrogen, to a solution of **4** or **5** (2 mmol) in anhydrous CH_2Cl_2 (40 mL) dry diisopropylethylamine (4 mmol, 0.74 mL) is added, followed by slow addition of freshly distilled iodotrimethylsilane (4 mmol, 0.54 mL). The brown mixture is stirred for 7 h (for **4**) or 3 h (for **5**). After warming to r.t., the mixture is concentrated and the product **6** isolated by column chromatography (42 cm × 4 cm) on basic alumina, eluting with EtOAc/petroleum ether bp 60–70 °C (1:2) or, for **6a,b**, silica (eluent $CHCl_3$ or EtOAc/petroleum ether bp 60–70 °C). For **6f**, additional purification is achieved using the Chromatotron (alumina, eluent EtOAc/petroleum ether bp 60–70 °C 1:10; Table).

1,3-Dithioles 8; General Procedure:
Compounds **8a–e** are preapared essentially by the procedure given above for the synthesis of **6**; however, after addition of the react-

ants at −78 °C, the mixture is allowed to warm to r.t. and is stirred for 2 h. On workup, prior to concentration, the reaction mixture is washed with water (1 × 20 mL) and products **8** purified using the Chromatotron (silica gel), eluent petroleum ether bp 60–70 °C (Table).

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