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Unusual Reduction of 2-Sulfolenes

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The reduction of 2,3,5-substituted 2-sulfolenes with sodium in EtOH leads to 4,5-dihydrothiophenes; the reduction of 2,3-substituted 2-sulfolenes leads to a mixture of 4,5-dihydrothiophenes and sulfolanes.

Dihydrothiophene-1,1-dioxides are known to be valuable synthons for the construction of various naturally occurring compounds.[1] Such syntheses usually involve a pyrolytic desulfonylation of suitably-substituted 3-sulfolenes leading to respective 1,3-dienes. The reductive desulfonylation of sulfolenes with the conservation of the endocyclic double bond position and geometry would allow us to obtain other unsaturated structures, for example, 1,4- and 1,5-dienes.

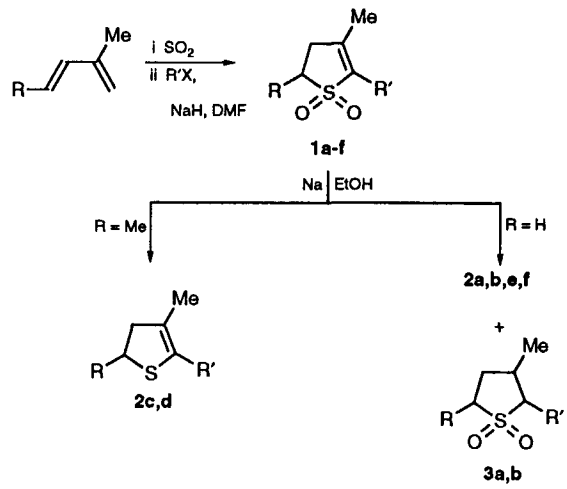
Earlier attempts at reduction were unsuccessful. Reduction with lithium in NH_3 led to mixtures of olefins,[2] and the action of $LiAlH_4$[3] and catalytic hydrogenation[4] both resulted in double bond hydrogenation. We investigated the reduction of 2-sulfolenes with sodium in ethanol, Scheme 1.†

It was found that the reduction proceeded regiospecifically giving 4,5-dihydrothiophenes **2** (20–40% yield) in the case of 5-substituted sulfolenes **1c,d**. Unexpectedly, the reduction of sulfolenes unsubstituted at position 5 gave mixtures of 4,5-dihydrothiophenes and sulfolanes [in 1:2 (a) and 1:2.5 (b) ratios] with combined yields *ca.* 40%. Yields of the reduction products were decreased probably due to sulfolene ring opening by an alcoholate anion.[1]

The reaction mixtures were separated by column chromatography and the products were identified by means of IR, ^{1}H NMR and mass spectroscopy. The ^{1}H NMR spectra of the starting materials and those of the products did not differ substantially.‡

† A solution of 5 mmol sulfolene in a mixture of 10 ml THF and 10 ml EtOH was stirred at room temperature. Pieces of sodium (*ca.* 0.03 g each) were added till their dissolvation ceased. After the addition of the last portion the reaction was quenched with EtOH. Then 10 ml H_2O was added, the solution was neutralizd with dilute H_2SO_4 and extracted with Et_2O (2 × 20 ml). The ether layer was dried with $MgSO_4$, concentrated *in vacuo* (except for **2e, 2f**) and chromatographed through a column with 25 g SiO_2 (Silpearl) (the gradient elution from hexane to Et_2O).

‡ In the ^{1}H NMR spectra (400 MHz) of dihydrothiophenes **2a,b** there were two connected multiplets C^4H_2 and C^5H_2 at 2.0 and 2.7 ppm (16 H each, ABMN system). In the spectra of starting sulfolenes the respective multiplets were shifted to 2.1 and 3.2 ppm, respectively. In the spectra of benzyl-substituted sulfolenes **1a,c** and sulfides **2a,c** the CH_2Ph signals were shifted to 3.64 and 3.48 ppm, respectively. The difference was smaller for the shifts of the CH_3–C^3 signal, which was equal to 1.75 ppm in the case of sulfolenes **1a–d** and 1.71 ppm in the case of sulfides **2a–d**.

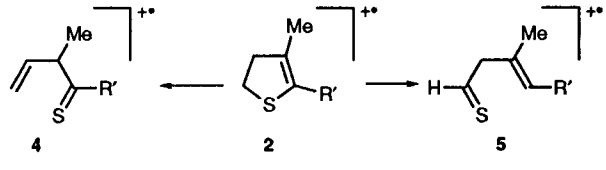


a R = H R' = $PhCH_2$
b R = H R' = $Me_2C{=}CHCH_2$
c R = Me R' = $PhCH_2$
d R = Me R' = $Me_2C{=}CHCH_2$
e R = H R' = Me
f R = H R' = CD_3

Scheme 1

Therefore, mass spectrometry was found to be the most useful method of structure confirmation.

The mass spectra of substituted 4,5-dihydrothiophenes have not so far been described. In the mass spectra of sulfides **2a–f** the peaks of the molecular ions are intense (40–100%), as previously observed for the unsubstituted dihydrothiophene.[5] The main fragmentation routes were connected with substituent loss. The presence of ions with *m/z* 62 (80%, CD_3CS) in the spectrum of **2f**, *m/z* 59 (62%, CH_3CS) in the spectrum of **2e**, *m/z* 135 (7%, $PhCH_2CS$) in the spectrum of **2a** and *m/z* 135 (11%, $PhCH_2CS$) in the spectrum of **2c** indicates the possibility of molecular ion rearrangement to structure **4**, Scheme 2.



Scheme 2

The abundance peaks with *m/z* 128 (20%, $[M-C_2H_6S]^{+\cdot}$), 129 (20%, $[M-C_2H_5S]^+$), 131 (20%, $[M-C_2H_3S]^+$) in the spectrum of **2a** allow us to propose the rearrangement of the molecular ion to the structure **5**. In the mass spectra of **2b** and **2d** the fragmentation processes in the R^1 substituents obscured the rearrangements of the dihydrothiophene ring. The sulfolane spectra exhibited intense molecular ion peaks. Further fragmentation was trivial ($M-SO_2H$, $M-SO_2H_2$), as previously observed for the unsubstituted sulfolane.[5]

In the IR spectra of products **2a–f** the characteristic bands of the SO_2 group were absent.

The sulfides **2** differ profoundly from the sulfones **1** and **3** in their chromatographic behaviour: R_f of the sulfides, 0.8–0.9; R_f of the sulfones **3**, 0.3–0.4; R_f of the starting sulfolenes, 0.2 (in hexane: ether, 1:1).

The sulfides **2e** and **2f** were detected among the products of **1e** and **1f** reduction by means of chromato-mass spectrometry.§

References

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§ *Mass spectra:* **2a** 2-Benzyl-3-methyl-4,5-dihydrothiophene (yield 11%), $M^{+\cdot}$ 190(49) 175(4) 159(10) 143(15) 135(7) 131(17) 129(17) 128(17) 117(20) 115(15) 99(42) 91(100) 77(15) 65(27) 55(10) 51(13).

2b 3-Methyl-2-(3-methylbut-2-enyl)-4,5-dihydrothiophene (yield 14%), $M^{+\cdot}$ 168(70) 142(12) 140(20) 126(14) 125(100) 112(12) 111(28) 107(16) 93(14) 92(17) 91(25) 85(12) 81(12) 79(22) 77(18) 71(15) 69(25) 67(13) 65(11) 59(12) 57(13) 55(23) 53(15).

2c 2-Benzyl-3,5-dimethyl-4,5-dihydrothiophene (yield 38%), $M^{+\cdot}$ 204(82) 135(11) 129(10) 128(10) 115(14) 113(35) 91(100) 71(14) 69(11) 65(13) 57(25) 55(18).

2d 3,5-Dimethyl-2-(3-methylbut-2-enyl)-4,5-dihydrothiophene (yield 15%), $M^{+\cdot}$ 182(24) 149(10) 140(18) 125(47) 111(26) 97(38) 95(30) 91(11) 85(35) 83(35) 81(30) 71(65) 69(60) 57(100) 55(60).

2e 2,3-Dimethyl-4,5-dihydrothiophene, $M^{+\cdot}$ 114(71) 113(47) 99(100) 98(14) 97(12) 85(12) 79(29) 77(13) 71(12) 65(24) 59(59) 58(20) 53(15) 51(11).

2f 3-Methyl-2-([$^2H_3$]methyl)-4,5-dihydrothiophene, $M^{+\cdot}$ 117(100) 116(70) 102(50) 99(80) 82(12) 71(20) 62(80) 58(18) 55(12).

3a 2-Benzyl-3-methyltetrahydrothiophene-1,1-dioxide (yield 18%), $M^{+\cdot}$ 224(35) 160(10) 159(46) 158(23) 157(10) 143(48) 131(36) 129(11) 117(43) 104(16) 92(12) 91(100) 81(29) 65(13) 55(15).

3b 3-Methyl-2-(3-methylbut-2-enyl)tetrahydrothiophene-1,1-dioxide (yield 35%), $M^{+\cdot}$ 202(73) 139(11) 137(18) 136(87) 135(24) 123(15) 122(13) 121(100) 119(11) 110(13) 109(73) 107(20) 96(11) 95(60) 94(15) 93(78) 92(22) 83(13) 82(24) 81(95) 80(31) 79(17) 77(13) 71(11) 69(80) 68(17) 67(53) 57(13) 55(47) 53(22).