Desulfonylation of α-Methylthio-α,β-unsaturated Sulfones. A New Route to One Carbon Homologation of Aromatic Aldehydes

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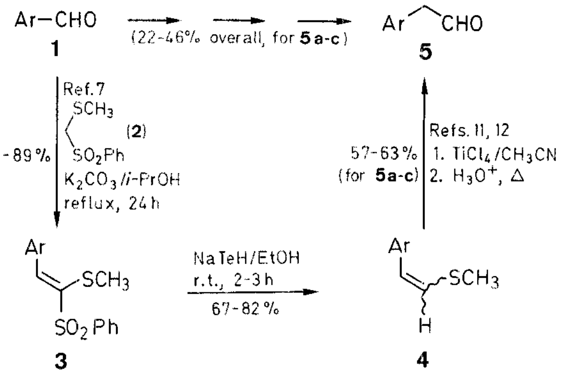
α-Methylthio-α,β-unsaturated sulfones **3** prepared from aromatic aldehydes **1** and sulfone **2** react with sodium hydrogen telluride in ethanol to undergo reductive desulfonylation to give vinyl sulfides **4** with certain extent of stereospecificity. A new route to one carbon homologation of aromatic aldehydes **1** to **5** is achieved by hydrolysis of **4** with titanium tetrachloride.

α-Methylthio-α,β-unsaturated sulfones **3** are important synthetic intermediates.[1-3] Recently, it has been reported that α-methylthio-α,β-unsaturated sulfones can be smoothly reduced to α-methylthio substituted sulfones by sodium borohydride.[3] Because sodium hydrogen telluride is a higher selective reducing agent than sodium borohydride, it has been used to reduce the C–C double bond of numerous α,β-unsaturated compounds.[4,5] We found[6] that sodium hydrogen telluride can selectively reduce the C–C double bond of α-sulfonyl-α,β-unsaturated ketones in ethanol/chloroform, whereas in dimethylformamide/ethanol, both reduction of C–C double bond and reductive desulfonylation are observed. In this paper we report on the reductivity of sodium hydrogen telluride toward α-methylthio-α,β-unsaturated sulfones **3**.

Sulfones **3** were readily prepared by the Knoevenagel condensation of aromatic aldehydes **1** with methylthiomethyl phenyl sulfone (**2**). Reaction of sodium hydrogen telluride with sulfones **3** in ethanol at room temperature effects a reductive desulfonylation to the unsaturated sulfides **4** preferentially, with the conjugated C–C double bond remaining unaffected.

This reductive desulfonylation possesses certain extent of stereospecificity. Starting from (*E*)- α-methylthio-α,β-unsaturated sulfones **3**,[7] desulfonylation affords *Z*-isomers of vinyl sulfides in major amounts (Table). The importance of vinyl sulfides as synthetic intermediates.[8,9] is illustrated by the aldehydrolysis of **4** to aldehydes **5**.[10-12]

In summary, we have shown that sodium hydrogen telluride can be used for preferential reductive desulfonylation of α-methylthio-α,β-unsaturated sulfones **3** to unsaturated sulfides **5**. The combination of reaction sequences starting from an aromatic aldehyde **1** via the vinyl sulfide **4** constitutes a new route to homologate aromatic aldehydes by one carbon atom.



1, 3, 4	Ar	1, 3, 4	Ar	5	Ar
a	Ph	d	3-ClC_6H_4	a	Ph
b	4-$CH_3C_6H_4$	b	4-$CH_3C_6H_4$	e	4-ClC_6H_4
c	4-$CH_3OC_6H_4$	f	2-furyl	c	4-$CH_3OC_6H_4$

(*E*)-α-Methylthio-α,β-unsaturated sulfones **3** were prepared by the method reported.[7]

The vinyl sulfides **4a–c** prepared (see below) were hydrolysed to the aldehydes **5a–c** as described in the literature,[11,12] and identified by IR and ^{1}H-NMR data.

Table. Vinyl Sulfides 4 Prepared[a]

Product	Yield (%)	Z/E-Ratio[b]	IR (neat)[c] ν(cm^{-1})	^{1}H-NMR (CDCl$_3$/TMS)[d] δ, J(Hz)
4a	82	74 : 26	1607, 1505, 847, 778, 740, 690, 530	Z-: 2.37 (s, 3H, CH$_3$S); 6.20, 6.43 (AB System, 2H, J = 10.8); 7.20–7.60 (m, 5H$_{arom}$) E-: 6.35, 6.80 (AB System, 2H, J = 15.8)
4b	73	74 : 26	1600, 1516, 820, 680, 523	Z-: 2.34 (s, 3H); 2.36 (s, 3H, CH$_3$S); 6.13, 6.37 (AB system, 2H, J = 10.8); 7.04–7.48 (m, 4H$_{arom}$) E-: 6.30, 6.69 (AB system, 2H, J = 15.5)
4c	75	68 : 32	1610, 1515, 850, 830, 784, 730, 680, 530	Z-: 2.36 (s, 3H, CH$_3$S); 3.8 (s, 3H, CH$_3$); 6.07, 6.39 (AB system, 2H, J = 10.8); 6.78–7.52 (m, 4H$_{arom}$) E-: 6.30, 6.62 (AB system, 2H, J = 15.4)
4d	78	76 : 24	1600, 1562, 1482, 830, 788, 770, 672, 560	Z-: 2.36 (s, 3H, CH$_3$S); 6.09, 6.33 (AB system, 2H, J = 11); 7.16–7.52 (m, 4H$_{arom}$) E-: 6.21, 6.83 (AB system, 2H, J = 15.4)
4e	80	68 : 32	1603, 1493, 1407, 1090, 1010, 847, 827	Z-: 2.37 (s, 3H, CH$_3$S); 6.24, 6.39 (AB system, 2H, J = 11); 7.20–7.50 (m, 4H$_{arom}$) E-: 6.26, 6.79 (AB system, 2H, J = 15.4)
4f	67	72 : 28	1647, 1610, 1457, 1154, 1086, 1018, 742, 690	Z-: 2.36 (s, 3H, CH$_3$S); 6.13, 6.37 (AB system, 2H, J = 10.8); 7.20–7.65 (m, 3H$_{arom}$) E-: 6.16, 6.77 (AB system, 2H, J = 15.6)

[a] The Z/E-mixtures of vinyl sulfides are obtained as oils. All are known compounds and characterized spectroscopically.

[b] Determined by 90 MHz spectra.

[c] Recorded on Perkin Elmer 683 spectrophotometer.

[d] Recorded on JEOL FX 90Q spectrometer. For E-isomers, the chemical shifts of only the olefinic protons are given.

Methyl (β-Chlorophenylethenyl) Sulfide (4d); Typical Procedure:

To a solution of NaHTe, prepared from Te (1.3 g, 10 mmol), NaBH$_4$ (0.9 g, 24 mmol) in EtOH (20 mL) under N$_2$ atmosphere, is added a solution of (E)-α-methylthio-β-(3-chlorophenyl)ethenyl phenyl sulfone (**3d**; 1.3 g, 4 mmol) in EtOH (30 mL), and the mixture is stirred at room temperature for 3 h. The reaction is quenched by the addition of water (30 mL), and the mixture is kept open to air to precipitate out the Te powder. After 1 h, the mixture is filtered and the filtrate is extracted with ether (3 × 30 mL). The combined ethereal solution is dried (MgSO$_4$), and concentrated to give the crude product **4d**, which is purified by column chromatography on silica gel using benzene as eluent; yield: 0.57 g (78 %); colorless oil; Z/E-ratio = 76 : 24 (Table).

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(1) Ogura, K. *Pure Appl. Chem.* **1987**, *59*, 1033.

(2) Ogura, K., Watanabe, J., Takahashi, K., Iida, H. *J. Org. Chem.* **1982**, *47*, 5404.

(3) Ogura, K., Ohtsuki, K., Takahashi, K., Iida, H. *Chem. Lett.* **1986**, 1597.

(4) Yamashita, M., Kato, Y., Suemitsu, R. *Chem. Lett.* **1980**, 847.

(5) Ramesh, M., Shanmugam, P. *Indian J. Chem. Sect. B* **1983**, *22*, 617.

(6) Huang, X., Zhang, H. *Synth. Commun.*, in press.

(7) Ogura, K., Yahata, N., Hashizume, K., Tsuyama, K., Takahashi, K., Iida, H. *Chem. Lett.* **1983**, 767, and references cited therein.

(8) Dieter, R.K. *Tetrahedron* **1986**, *42*, 3029.

(9) Corey, E.J., Shulman, J.I. *J. Org. Chem.* **1970**, *35*, 777.

(10) Carlo, B., Giulio, C., Serafino, G. *Chim. Ind. (Milan)* **1977**, *59*, 839; *C.A.* **1978**, *88*, 152172.

(11) Mukaiyama, T., Fukuyama, S., Kumamoto, T. *Tetrahedron Lett.* **1968**, 3787.

(12) Mukaiyama, T., Kamio, K., Kobayashi, S., Takei, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3723.