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Direct Synthesis of Sulfines by Oxidation of Enethiolizable Thioketones

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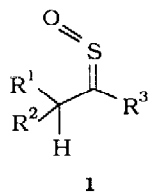
Abstract - Reaction of enethiolizable thioketones **2** with one equivalent of *meta*-chloroperoxybenzoic acid affords quantitatively the corresponding *E* sulfines **1** In contrast to literature expectations, direct synthesis of aliphatic sulfines by oxidation of thiocarbonyl compounds is thus possible, no divinyl disulfide **4** has been formed

Sulfines **1** are reactive heterocumulenes, for which a variety of synthetic routes has been developed (1-5) Direct oxidation of thiocarbonyl compounds **2** is limited to aromatic, non enethiolizable and α-unsaturated cases (2, 6-11) Our group has recently reported (12) that reaction of enethiolizable dithioesters with *meta*-chloroperoxybenzoic acid (*m*CPBA) gives the corresponding sulfines, whose stabilities have been studied In the case of thioketones, the literature predicts (2, 5, 13, 14) the formation of divinyl disulfides **4** Intrigued by these expectations and needing aliphatic sulfines for synthetic purposes, we revisited this oxidation



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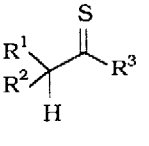

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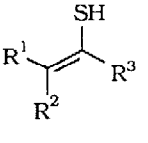

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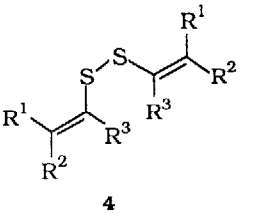


4

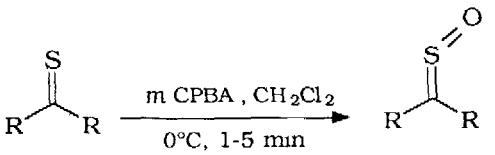
Aliphatic thioketones **2** are highy enethiolizable. Their enethiols **3**, which can be isolated, are isomerically stable (15, 16). Therefore we were especially eager to know the oxidation course for **2** sulfines **1** or divinyl disulfides **4** Only one case has so far been reported Duus and Carlsen (17) oxidized a β-thioxoketone and obtained a divinyl disulfide

For simplicity we first examined the oxidation of symmetric aliphatic thioketones **5** and **6** We carefully checked that our starting materials were devoid of isomeric enethiols **3** Reaction with one equivalent of *meta*-chloroperoxybenzoic acid (*m*CPBA) at 0°C in dichloromethane leads to immediate loss of the red thioketone colour To our surprise the products exhibited NMR signals that are characteristic of sulfines **7** and **8**

1) large upfield shift of protons located α and trans to the C=S group

2) the ^{13}C shifts of C=S=O are observed at *ca* 220 ppm

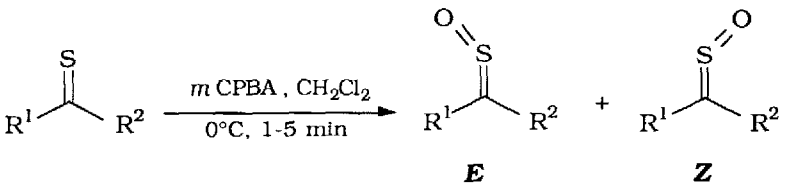
The reaction is quantitative We did not observe any divinyl disulfide **4**



5 R = iPr **7**

6 R = nC_6H_{13} **8**

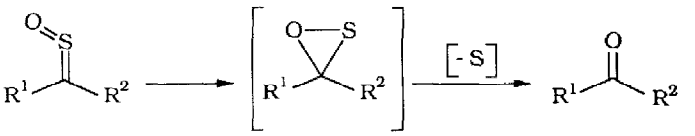
This prompted us to examine the oxidation of unsymmetrical thioketones **9-14** Their reaction with *m*CPBA under the same conditions furnishes quantitatively the sulfines **15-20**



E ***Z***

	R^1	R^2		*E* / *Z* ratio
9	Me	nC_5H_{11}	**15**	100 0
10	Me	tBu	**16**	100 0
11	Me	sBu	**17**	80 20
12	nC_5H_{11}	iPr	**18**	67 33
13	Et	Pr	**19**	50 50
14	Et	2-Methylbutyl	**20**	50 50

The oxidation reaction is highly regioselective in the case of the two compounds **9** and **10**, bearing a methyl group and an alkyl group, for which *E* sulfines **15** and **16** were formed Delivery of oxygen thus occurs on the side of this methyl substituent and opposite to the bulky tertiobutyl group More surprising is the selectivity observed with R^1 = Me and R^2 = nPentyl Other thiones **11-14**, bearing various groups, led to mixtures of *E* and *Z* isomers We have detected no variation in these ratios We believe that these compounds result from kinetic control and that these sulfines are configurationally stable, in contrast with those sulfines obtained from dithioesters (12) that isomerize rapidly Stereochemical assignments of compounds **15** to **18** have been achieved by lanthanide induced shifts through complexation with $Eu(fod)_3$ (18) and analogy with sulfine **7** The thermal stabilities of sulfines were examined at room temperature After some days elemental sulfur is formed and corresponding ketones **22-29** are produced quantitatively These observations may be explained by formation of intermediate oxathiiranes **21** arising from thermally allowed electrocyclization of sulfines (2, 19, 20) followed by sulfur extrusion (2, 21)



7, 8, 15 - 20 **21** **22 - 29**

Our results stand in sharp contrast with literature expectations no divinyl disulfide **4** was formed We have achieved for the first time the direct oxidation of enethiolizable thioketones It occurs with a noteworthy selectivity in favour of the *E* isomer

These reactions provide an easy entry to aliphatic sulfines They can now be used for organic synthesis within the limit of their thermal stabilities We are presently looking at their behaviour

References

1 Duus, F In *Comprehensive Organic Reactions The Synthesis and Reactions of Organic Compounds*, Barton, D H R , Ollis, W D , Neville Jones, D , Eds , Pergamon Oxford, 1979, Vol 3, p 373-487.

2 Zwanenburg, B *Recl Trav Chim Pays-Bas* **1982**, *101*, 1-27

3 Zwanenburg, B , Lenz, B G In *Houben-Weyl Methoden der Organischen Chemie*, Klamann, D , Ed , Thieme Stuttgart, 1985, Band E11, Teil 1, p 911-949

4 Zwanenburg, B *Rev Heteroatom Chem* **1988**, *1*, 218-234

5 Zwanenburg, B *Phosphorus, Sulfur Silicon Relat Elem* **1989**, *43*, 1-24

6 Strating, J , Thijs, L , Zwanenburg, B *Tetrahedron Lett* **1966**, 65-67

7 Zwanenburg, B , Thijs, L , Strating, J *Recl Trav Chim Pays-Bas* **1967**, *86*, 577-588

8 Ohno, A , Nakamura, K , Uohama, M , Oka, S *Chem Lett* **1975**, 983-984

9 Bonini, B F , Mazzanti, G , Zani, P , Maccagnani, G *J Chem Soc , Perkin Trans 1* **1989**, 2083-2088

10 Pushkara Rao, V , Ramamurthy, V *Synthesis* **1985**, 526-527

11 Motoki, S , Toba, Y , Karakasa, T , Saito, T *Chem Lett* **1988**, 319-322

12 Metzner, P , Pham, T N *J Chem Soc , Chem Commun* **1988**, 390-391

13 van der Leij, M , Zwanenburg, B *Tetrahedron Lett* **1978**, 3383-3386

14 Porskamp, P A T W , van der Leij, M , Lammerink, B H M , Zwanenburg, B *Recl Trav Chim Pays-Bas* **1983**, *102*, 400-404

15 Paquer, D , Vialle, J *Bull Soc Chim Fr* **1969**, 3595-3601

16 Paquer, D , Vialle, J *Bull Soc Chim Fr* **1971**, 4407-4410

17 Carlsen, L , Duus, F *Synthesis* **1977**, 256-258

18 Tangerman, A , Zwanenburg, B *Tetrahedron Lett* **1973**, 79-82

19 Karlstrom, G , Roos, B O , Carlsen, L *J Am Chem Soc* **1984**, *106*, 1557-1561

20 Carlsen, L , Harrit, N , Holm, A *J Chem Soc , Perkin Trans 1* **1976**, 1404-1407

21 Carlsen, L , Holm, A , Koch, E , Stilkerieg, B *Acta Chem Scand , Ser B* **1977**, *31*, 679-682

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