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AN EFFICIENT AND MILD CLEAVAGE OF THIOL ACETATE WITH CLAYFEN IN THE ABSENCE OF SOLVENT*

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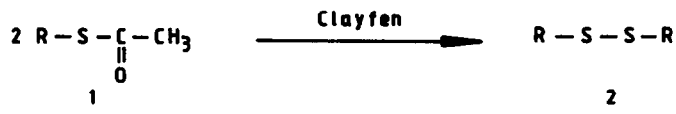
Abstract : The disulphides are synthesised through the mild cleavage of thiol acetate with clayfen in the absence of solvent.

Major advances in the synthesis of disulphides have been made during last decades from thiol derivatives[1]. This is mainly because of the less succeptibility of thiol derivatives for air oxidation. This is also important in multistep synthesis of peptides[2] and bioactive molecules[3] with disulphide bond.

Recently, the organic transformations using clay supported catalyst[4,5] is an area of growing interest due to ease of handling and workup. In particular the clayfen has become an effective oxidizing catalyst for the oxidation of alcohols[6] and cleavage of C=N bond[7]. In the course of our studies[8] in the application of clay in organic synthesis, herein we wish to report the oxidative cleavage of thiol acetate into disulphides with clay supported ferric nitrate in the absence of solvent.



1 2

R = aryl , alkyl

Table 1. Thiol Acetate into Disulphides

Entry	Thiol acetate (1)	Time (h)	Disulphide[a](2)	Yield (%)
a.	$C_6H_5SCOH_3$	3	$(C_6H_5S)_2$	92
b.	$CH_3(CH_2)_{10}SCOCH_3$	4	$[CH_3(CH_2)_{10}S]_2$	89
c.	$C_2H_5SCOCH_3$	3	$(C_2H_5S)_2$	87
d.	$AcO(CH_2)_2SCOCH_3$	5	$[AcO(CH_2)_2S]_2$	80
e.	CH_2-CH_2SCOCH_3 CH_2-CH_2SCOCH_3	4		50

[a]All products were characterised by spectroscopic data and by comparison with authentic samples.

In a typical procedure, thiol acetate **1a** 1.1 g (0.01 mol) and clayfen (3 g) was mixed in mortar and pestle. It was kept (3 h) with occasional mixing. Then extracted with dichloromethane (3x20 ml) and washed with water. The organic layer was dried over sodium sulphate and solvent removed under vacuum. The residue upon purification by column chromatography yielded diphenyl disulphide **2a** in 92%.

The added importance of this procedure is that it does not require the solvent for reaction and is thus advantageous. This nonsolvent feature of the reaction may allow in the solid phase peptide synthesis.

In conclusion, we believe that the experimental simplicity and the mildness of the reaction conditions should allow the application of this methodology for the preparation of wide range of biologically active disulphide bond containing compounds.

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REFERENCES

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1. Sata, T.; Otera, J. and Nosuki, H. Tetrahedron Lett. **1990**, 31, 3595; Wolmon, Y. "The Chemistry of the Thiol Groups", ed. by Patai, S. John Wiley & Sons, London, 1974, Chapter 14.
2. Bodanszky, M. "Principles of Peptide Synthesis", Springer-Verlag, Berlin, **1984**, Chapter 4.
3. Johnson, J.R.; Bruce, W.F. and Dutcher, J.D. J. Am. Chem. Soc., **1943**, 65, 2005; Miller, P.A.; Milstrey, K.P. and Trown, P.W. Science, **1968**, 159, 431.
4. Laszlo, P. Acc. Chem. Res., **1986**, 19, 121; Theng, B.K.G. "The Chemistry of Clay Organic Reactions", Adams Hilger, London, **1974**.
5. Pinnavaia, T.J. Science, **1983**, 220, 365.
6. Laszlo, P. and Cornelis, A. Synthesis, **1980**, 849.
7. Laszlo, P. and Polla, E. Tetrahedron Lett. **1984**, 25, 3309; Laszlo, P. and Polla, E. Synthesis, **1985**, 439.
8. Meshram, H.M. Synthetic Commun. **1990**, 20, 3253; Meshram, H.M. Synthesis, **1992**, 943; Meshram, H.M. Org. Prep. Proced. Int. (In press).

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