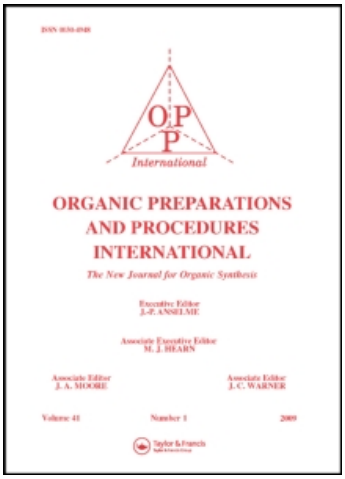

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IMPROVED AND CONVENIENT SYNTHESIS OF DISULFIDES IN THE ABSENCE OF SOLVENT CATALYZED BY CLAYFEN

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IMPROVED AND CONVENIENT SYNTHESIS OF DISULFIDES IN THE ABSENCE OF SOLVENT CATALYZED BY CLAYFEN†

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Disulfides are important from both biological and practical points of view.[1] Moreover, the disulfides are used in sulfenylation[2] of enolates and other anions. The several methods[3,4] which have been developed for the oxidation of thiols into disulfides, require purification and use of solvent for reaction. More recently, the disulfides have been synthesized using Clayfen and hydrocarbon solvent with heating. However, the large scale manufacture of disulfides is usually fraught with difficulties because of the need for greater quantities of solvent and bigger reactors. Thus, there still is a need for a convenient and economically viable procedure.

Recently, more emphasis has been given to solid-phase reactions[6] because of their effectiveness and absence of solvent. The growing interest in the clay,[7] clay supported catalyst[8] and non-solvent prompted us to synthesize disulfides using Clayfen in the reactions absence of solvent. The yield and purity obtained in the non-solvent reaction is much better than the reported method.[5] Moreover, the quantity of catalyst used is less compared to an earlier procedure.[5]

TABLE. Oxidation of Thiols to Disulfides

R	Reaction time (hrs)	Yield[a] (%)	mp (bp)[b] (°C)	lit.[c] mp (bp) (°C)
C_6H_5	2	99	60	61-62
4-ClC_6H_4	1.5	99	70-71	71
4-CH_3C6H_4	2	98	46	46
2-$NH_2C_6H_4$	1	92	91-92	93
$C_6H_5CH_2$	2.5	96	72	71-72
$CH_3(CH_2)_{10}CH_2$	3	91	32	31-34[d]
HO-CH_2CH_2	3	80	(159-161/01)	(160-162/01)[e]
C_2H_5	2	94	(152-153)	(154)
n-C_4H_9	2	95	(224-226)	(226)

a) All products are characterized by mass, NMR, mp, bp and gave correct HRMS. b) Crystallized from ethanol. c) Ref. 9 unless otherwise noted. d) Ref. 10. e) Ref. 11.

$$\underset{\mathbf{1}}{2R-SH} \xrightarrow{\text{Clayfen}} \underset{\mathbf{2}}{R-S-S-R}$$

The high yields obtained under mild conditions and its applicability to functionally substituted thiols, coupled the absence side-reactions and the fact that no solvent is required makes the present

procedure economically useful for the large scale synthesis of symmetrical disulfides.

EXPERIMENTAL SECTION

General Procedure.- The thiol (0.01 mol) was mixed with Clayfen[12] (3 g) in mortar-pestle and kept at room temperature for 1-3 hrs with occasional mixing. The paste was then extracted with dichloromethane (3 x 30 mL) and the extract was dried over anhydrous sodium sulfate. Evaporation of the solvent gives pure **2** according to ^{1}H NMR and tlc analysis.

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