Kaolinitic Clay Catalyzed Reaction of Sulfur Monochloride with Aromatics: An Efficient and High Yield Synthesis of Symmetrical Disulfides

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Kaolinitic clay efficiently catalyses the reaction of sulfur monochloride with arenes to yield symmetrical 4,4' arene disulfides in a single step under heterogeneous phase.

The disulfides are a class of sulfur compounds possessing unique and rich chemistry in synthetic and biochemical area. For example, large disulfide-linked aggregates are prevalent in proteins and many other bioactive molecules.[1] Industrially, disulfides find wide applications as vulcanizing agents for rubbers and elastomers, giving them excellent tensile strength.

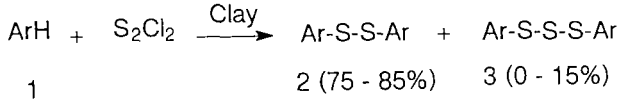
Preparation of disulfides generally involve the photochemical and electrochemical oxidation of thiols.[2] However, such methods generally lead to overoxidation and are scarcely used for preparative purposes. Another common method involves the catalytic oxidation of thiols in the presence of various catalysts like tetraazoannulene cobalt, tetrabutylammoniumcericnitrate, coenzyme PQQ, diselenide salt, iodylbenzene, DMSO, poly(vinyl pyridine) supported silver chromate etc. .[3] The cleavage of thiol acetates with clayfen[4] and the oxidation of alkyl halide with tetrathiometallates of both molybdenum and tungsten[5] leading to the formation of disulfides have also been well documented. However, these methods, being indirect involving preparation of thiol and subsequent oxidation with catalysts, are not viable.

A comprehensive literature search reveals that S_2Cl_2 has been known to react with activated substrates such as phenols and alkenes in the presence of a base, to yield disulfides in moderate yields.[6] However, the method suffers from severe disadvantages such as long reaction times (50 h), the use of large excess of substrates etc.

Further, use of $AlCl_3$ in stoichiometric amounts in order to catalyze the reaction of S_2Cl_2 with benzene results in moderate yields of monosulfide along with formation of thiophenol and thioanthrene.[7] Hence, there is a need to develop heterogeneous catalytic and efficient method for the preparation of disulfides.

Currently acid catalysis of organic transformation is an area of high potential and interest. Due to their Bronsted and Lewis acidities, clays function as efficient catalysts for a variety of organic transformations.[8] With this background in mind a systematic study of reaction of S_2Cl_2 with aromatics catalysed by solid acid catalyst such as clay was undertaken, the preliminary results of which are reported here.

When sulfur monochloride is reacted with aromatics in the presence of kaolinitic clay catalyst, a high yield of symmetrical 4,4' disulfides is obtained, along with minor amounts of trisulphides (Scheme 1).



Scheme 1.

Table 1 lists the results of various substrates which were converted into disulfides with S_2Cl_2 catalysed by kaolinitic clay.

Table 1. Clay catalyzed reaction of S_2Cl_2 with aromatics

Entry	Substrate	Product[a]	Yield %	
			Disulfide	Tri-sulphide
1.	Benzene	Diphenyl disulfide	70[c]	15
2.	Toluene	4,4'Ditolyl disulfide	65	10
3.	Chlorobenzene	4,4'-Dichlorophenyl disulfide	76	10
4.	Naphthalene	2,2'-Dinaphthyl disulfide	75	15
5.	Anisole	4,4'-Dimethoxyphenyl disulfide	78[b]	5
6.	Biphenyl	4,4'-Bis diphenyl disulfide	68	10
7.	Anthracene	2,2'-Dianthracenyl disulfide	68	10
8.	Thiophene	2,2'-Dithienyl disulfide	80[b]	10
9.	Cyclohexene	2,2'Dichloro dicyclohexyl disulfide	80	0

[a] Products were characterised by IR, NMR, Mass and microanalysis.
[b] Reaction proceeded at room temperature.
[c] The catalyst was recycled three times without any loss of activity.

From the Table 1 it is evident that the conversions are nearly quantitative in all substrates studied. In the absence of the catalyst, no reaction took place. A remarkable feature of this method is that a regiospecific formation of 4,4'-disulfides have been observed. (see entries 2-6) in Table 1. 2,2'-disulfides are not formed possibly due to steric crowding of the substrates experienced inside the β interlamelar space of the clay. The reaction also proceeds well with unactivated substrates such as benzene and toluene. With cyclohexene as the substrate, a high yield of 2,2'-dichlorodicyclohexyl disulfide (80 %) was obtained and no formation of trisulfide was observed. However, it may be noted that other solid catalysts such as HZSM-5, Hβ, HY and SiO_2, Al_2O_3 have failed to activate S_2Cl_2 with aromatic substrates. The catalyst

was recovered by filtration and successfully reused at least three times in the case of benzene without any loss of activity. The enhanced catalytic activity of acid activated clay could be attributed to the significant amount of acidity derived from Al^{3+}, Fe^{2+} and Ti^{2+} ions leached from the octahedral layer of the clay structure during acid leaching.[9] The sulfur monochloride coordinates well with the Al^{3+} present in the clay and thereby getting activated so that the electrophiles attacks the aromatic nucleus leading to the formation of disulfides.

In conclusion, our methodology offers a cheap, mild, neutral and environmentally friendly approach for the preparation of disulfides in a single step and in high yields.

The Kaolinitic clay was procured from the Padappakara mine of Quilon District, Kerala, India. It was subsequently purified, calcined and treated with acid (2M HCl) as reported elsewhere.[9] The clay has been thoroughly characterized by XRD, UV, ESR, SEM, EDX and chemical analysis. The chemical component of the clay was determined by wet chemical analysis (in %) SiO_2 = 67.45, Al_2O_3 = 22.20, TiO_2 = 3.45, Fe_2O_3 = 6.1 and K = 0.8.

To a mixture of substrate(10 mmoles) and clay catalyst(5 % w\w) in ethylene dichloride (20 mL) was added S_2Cl_2 (5 mmoles) dropwise. It was then refluxed for 2 h. After reaction was complete (TLC), the catalyst was filtered off and solvent removed. The crude reaction mixture was purified by column chromatography (SiO_2). Products were characterised by ^1H NMR, Mass and microanalysis.

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10 2,2'-Dithienyl disulfide: mp 48 °C. ^1H NMR (200 MHz, $CDCl_3$); δ 7.50 (m, 2H), 7.25 (m, 2H), 7.00 (m, 2H). MS m/z (rel. intensity) 230 (M^+, 42), 198 (30) , 166 (10) , 147 (17), 115 (95), 71 (100), 64 (5).
2,2'-Dichlorodicyclohexyl disulfide; Oil, ^1H NMR (200 MHz, $CDCl_3$); δ 1.10 (s, 4H, 2 x CH_2) , 1. 5 (s, 8H, 4xCH_2), 2.10 (s, 4H, 2xCH_2), 3.0 (m, 2H, 2xCH_2), 4.0 (M, 2H, 2xCH). MS m/z (rel. intensity): 298 (M+, 10), 266 (10), 231 (11), 182 (3), 149 (2), 116 (5), 80 (100), 67 (13), 53 (19).
Diphenyl disulphide: mp 60 °C. ^1H NMR (200 MHz, $CDCl_3$); δ 7.2 (6H, m, CH), 7.6 (4H,m, CH), MS m/z (rel. intensity) 250(M^+, 30), 218 (70), 185 (20), 154 (20), 141 (62), 109 (100), 77 (40), 69 (32)
Bis biphenyl disulphide: mp 66°C. ^1H NMR (200 MHz, $CDCl_3$); δ 7.5(18 H, m, CH). MS m/z (rel. intensity) 370 (M^+, 20), 338 (80), 256 (20), 192 (20), 185 (80), 152 (50) , 64 (100).
Dinapthyldisulphide: mp 73 °C. ^1H NMR (200 MHz, $CDCl_3$); δ 7.6 (10 H, m, CH). 8.6 (4H) MS m/z (rel. intensity) 318 (M^+,40), 286 (15), 254 (10), 190 (25), 159 (95), 115 (100), 64 (22).
4,4'Dichlorophenyldisulphide: mp 69-71°C. ^1H NMR (200 MHz, $CDCl_3$); δ 7.4 (8H, m, CH). MS m/z (rel. intensity) 286 (M^+, 10), 256 (52), 84 (49), 108 (65), 75 (60), 64 (100).
4,4'Dimethoxyphenyldisulphide: mp 46 °C. ^1H NMR (200 MHz, $CDCl_3$); δ 6.9(4H, d, J= 10 Hz,CH), 7.4 (4H, d, J= 10 Hz), 3.6 (6H, s, 2xCH_3). MS m/z (rel. intensity) MS m/z (rel.intensity) 278 (M+, 10), 246 (100), 231 (50), 171 (20), 139 (30), 63 (30).
Dianthracenyldisulphide: mp 85 °C. ^1H NMR (200 MHz, $CDCl_3$); δ 7.6 (9H, d, J= 15 Hz), 8.5 (9H, d, J= 15 Hz), MS m/z (rel. intensity) 418 (M+, 5), 260(40), 209(20), 176(50), 123(40), 88(40).