Synthesis of organic sulfides from thiols using montmorillonite–3-aminopropyltriethoxysilane as a new catalyst

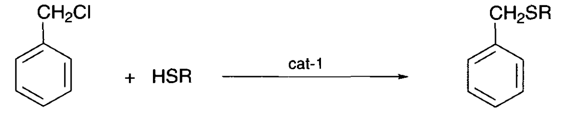
P. Kannan,[a] K. Pitchumani,*[a] S. Rajagopal†[a] and C. Srinivasan[b]

[a] *School of Chemistry, Madurai Kamaraj University, Madurai-625 021, India*
[b] *Department of Materials Science, Madurai Kamaraj University, Madurai-625 021, India*

A new basic clay, synthesised by introducing 3-aminopropyltriethoxysilane into montmorillonite, catalyses the reaction between benzyl chloride and thiols to afford high yields of the corresponding sulfides.

Although clays have mainly been employed as acid catalysts,[1] a few reports[2–5] have appeared on the reactions catalysed by basic clays. For the past two decades we have been interested in the thermal and photochemical redox reactions of organic sulfides.[6,7] As we require for such studies different types of organic sulfides, we have looked for a convenient method for the synthesis of benzyl sulfides of general formula $ArCH_2SR$. Here we report a simple and convenient method for the synthesis of several such organic sulfides, by the reaction between benzyl chloride and thiols (shown in Scheme 1) in the presence of a modified montmorillonite clay containing 3-aminopropyltriethoxysilane (cat-1). Some of these compounds are reported for the first time.

The catalyst was prepared by refluxing 5 g of sodium-exchanged clay with 50 cm^3 of 0.3 mol dm^{-3} 3-aminopropyltriethoxysilane in water for 38 h. The clay was then filtered, washed thoroughly with distilled water and dried at 95 °C for 7 h. The pH of the clay was checked by pH meter (clay in suspension in distilled water) and found to be around 8.7–9.2. Even after three to four months the pH of the clay remains the same. FT-IR of the clay sample clearly shows the stretching frequency of the alkyl chain and primary amino group.



R = C_6H_5, p-$MeOC_6H_4$, p-ClC_6H_4, C_4H_9, C_6H_{13}, C_8H_{17}

Scheme 1

Table 1 Reaction conditions used and yields of sulfides ($ArCH_2SR$)

Entry	R	Reaction conditions	Yield (%)
1	Ph	95 °C for 5 min	75
2	p-$MeOC_6H_4$	95 °C for 12 h	12
3	p-ClC_6H_4	95 °C for 30 min	83
4	$Me(CH_2)_3$	95 °C for 2.5 h	77
5	$Me(CH_2)_5$	95 °C for 8 h	84
6	$Me(CH_2)_7$	95 °C for 10 h	69
7	Ph	room temp. for 2 h	12
8	Ph	in 50 cm^3 EtOH, 95 °C, 15 min	64
9	Ph	95 °C for 90 min[a]	49
10	Ph	95 °C for 2 h[b]	—
11	Ph	stirring for 90 min, then reflux in steambath with NaOEt for 2 h[c]	60

[a] In 0.3 mol dm^{-3} (0.3 cm^3) 3-aminopropyltriethoxysilane without clay. [b] Blank experiment (without solvent and catalyst *i.e.* just mixing two reagents). [c] In homogeneous media (lit.,[8] value).

In a typical experiment the catalyst (2 g) and substrates (benzyl chloride and thiols) were taken in equimolar ratio (8.68 × 10^{-3} mol dm^{-3}), mixed well and heated in a water bath. The progress of the reaction was checked by TLC. After completion of the reaction, the reaction mixture was extracted with diethyl ether. The residue after the removal of the ether was analysed in a Shimadzu LC-8A hplc system [reverse phase column (ODS), UV-detector at 258 nm, 70% methanol as mobile phase]. The product was confirmed by FTIR, 200 MHz ^{1}H NMR and elemental analysis. The other by-product, HCl, was formed as gas. The formation of HCl did not affect the catalytic activity of the clay, which was evident from the similar results observed when the clay was reused. The same reaction was carried out in ethanol medium as well as at room temperature (details are given in Table 1). Although similar products are obtained in both cases, the reaction rate is slow at room temperature. When a blank experiment containing no clay was carried out, no product was obtained.

This reaction, studied for the first time on heterogeneous media, mainly depends on the basicity of modified clay, the ability to remove the proton from the corresponding thiols and the nucleophilicity of the benzenethiolate ion. Here, we have used three aromatic thiols (containing electron withdrawing and electron releasing groups) as well as three aliphatic thiols. With aromatic thiols containing electron releasing groups, *e.g.* *p*-methoxybenzenethiolate, the reaction rate is very slow (*i.e.* even after 12 h only 12% conversion has taken place). This is because the removal of the proton is very difficult. In the case of thiols containing electron withdrawing groups, *e.g.* *p*-chlorobenzenethiol, the reaction rate is faster compared with the thiol bearing an electron releasing substituent, but slower than the parent benzenethiol. Here, even though the proton removal is easier, the nucleophilicity of the *p*-chlorobenzenethiolate ion is lower than that of benzenethiol.

In the case of the reaction of aliphatic thiols of increasing chain length, *e.g.* butane, hexane and octane, the rate of the reaction decreases with the increase in the length of the alkyl chain. This may be attributed to the increase in the electron releasing capacity with increasing length of the chain and also due to the difficulty of entry of long chain thiols into the clay interlayer. In general, compared to aromatic thiols, aliphatic thiols take more time to react. The reaction conditions and percentage of sulfide formed are shown in Table 1. The clay catalysed reaction is superior to the reaction in the homogeneous medium because the organised assembly of aluminosilicate layers leads to a quantitative yield of products in a very short time. The reaction studied here is also convenient to carry out since the catalyst can be easily filtered off and reused several times, giving similar yields.

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Footnote

† To whom correspondence should be addressed.

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