

Syntheses of organic benzyl sulphides from thiols using a modified clay catalyst

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MS received 5 April 1999; revised 7 June 1999

Abstract. The reaction between benzyl chlorides and thiols is catalysed efficiently by a new basic clay, Cat-1 prepared by introducing 3-aminopropyltriethoxysilane into clay interlayers of K-10 and KSF montmorillonites, as well as bentonite clays affording high yields of the corresponding sulphides.

Keywords. Basic clay catalyst; benzyl sulphides; synthesis.

1. Introduction

Clays, a class of layered aluminosilicates¹ have residual negative charge in the framework and exchangeable cations which can be suitably modified to gain control over the acidity/basicity. They are extensively employed as acid catalysts¹. However, only a few reports²⁻⁵ have appeared on reactions catalysed by basic clays. Our interest in thermal and photochemical redox reactions of organic sulphides, prompted us to search for suitable new methods for their syntheses. Herein, we report a detailed account of a very simple, convenient and general method for the syntheses of benzyl sulphides of general formula ArCH_2SR (1), by the reaction between benzyl chloride and thiols (shown in scheme 1) in the presence of a modified montmorillonite clay (Cat-1) containing 3-aminopropyltriethoxysilane (3-APTES). Preliminary results of this account are already communicated⁶. A schematic representation of preparation of the catalyst (detailed procedure in §2) is given in chart 1.

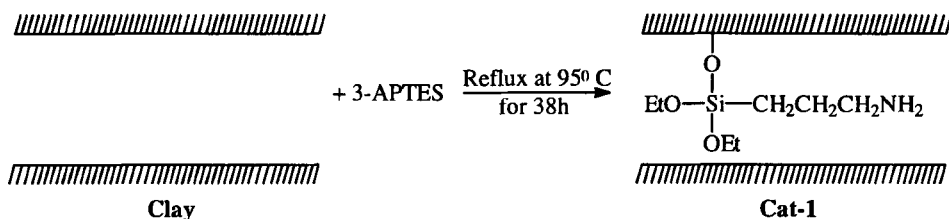


Chart 1.

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2. Experimental

2.1 Preparation of the catalyst

Cat-1 was prepared by refluxing 5 g of sodium-exchanged clay (K10-montmorillonite and bentonite from Aldrich and KSF-montmorillonite from Fluka) with 50 cm³ of 3-APTES (0.3 mol dm⁻³) 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, as a suspension in distilled water (0.2 g of Cat-1 in 100 ml of water, sonicated for 15 min), was checked by pH meter (and also by Hammett indicators) and found to be around 8.7–9.2. Even after three to four months, the pH, remains the same. FT-IR of the sample (figure 1) clearly shows the stretching frequency of the alkyl chain and the primary amino group.

2.2 Reaction procedure

In a typical experiment a 1:1 mixture of benzyl chloride and thiol (8.68×10^{-3} mol dm⁻³ each) was mixed well with the catalyst (2 g) and heated as a solid mixture 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 products were isolated in some cases and confirmed by FT-IR, 200 MHz ¹H-NMR and ¹³C-NMR spectra. In other cases identification was done by HPLC.

2.3 Spectral data of sulphides

The NMR data of the compounds are listed below.

- ¹H-NMR of C₆H₅ CH₂ S C₆H₅ : 7.3 δ (10H, *m*), 4.15 δ (2H, *s*), IR: 3050, 2960, 680 cm⁻¹;
- ¹H-NMR of C₆H₅ CH₂ S C₆H₄-*p*-Cl: 7.4 δ (9H, *m*), 4.2 δ (2H, *s*);
- ¹H-NMR of C₆H₅ CH₂ S C₆H₄-*p*-OCH₃: 6.8–7.4 δ (9H, *m*), 4.1 δ (2H, *s*), 3.8 δ (3H, *s*);
- ¹H-NMR of *p*-OCH₃-C₆H₄ CH₂ S C₆H₄-*p*-Cl: 6.76–7.34 δ (8H, *m*), 4.15 δ (2H, *s*), 3.76 δ (3H, *s*);
- ¹H-NMR of *o*-NO₂-C₆H₄ CH₂ S C₆H₄-*p*-Cl: 7.8–7.6 δ (1H), 6.9–7.3 δ (7H, *m*), 4.25 δ (2H, *s*).

Syntheses of all sulphides except **1n** and **1o** (table 1) are reported⁸. Sulphide **1o** was isolated and characterized by its NMR spectra. Since the yield of **1n** is very low, it is not isolated for characterization. Monobenzylated as well as dibenzylated derivatives of 3,4-toluenedithiol (MI peaks at 246 and 336 mass units respectively) and monobenzylated 1,3-propanedithiol (MI peak at 198 mass units) were identified by GC-MS.

3. Results and discussion

The clay-catalysed reaction between benzyl chlorides and thiols is found to be general and a wide range of aliphatic thiols, dithiols and substituted benzyl chlorides can be employed (scheme 1). Not only K10-montmorillonite but also KSF-montmorillonite and

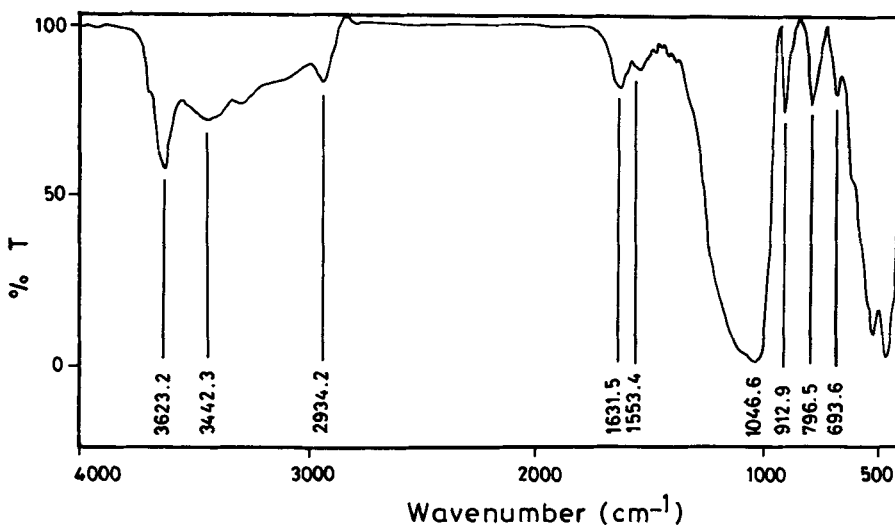
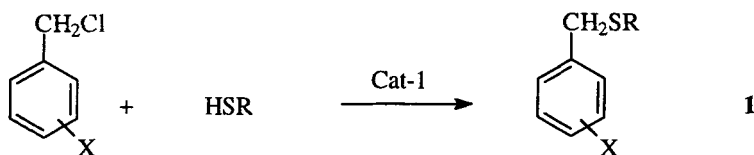


Figure 1. FT-IR spectrum of 3-APTES-pillared K 10-montmorillonite.

bentonite clays can be used. Here, we have employed three aromatic (containing electron-withdrawing and electron-releasing groups) as well as three aliphatic thiols. With aromatic thiols containing electron-releasing groups, e.g. *p*-methoxythiophenol, the reaction rate is very slow, i.e. even after 12 h, there is only about 12% conversion indicating that the removal of proton from the thiol is very difficult in this case.

With thiols containing electron-withdrawing groups, e.g. *p*-chlorothiophenol, the reaction rate is faster compared to a thiol bearing an electron-releasing substituent but slower than the parent thiophenol. Here, even though proton removal is easier, the nucleophilicity of *p*-chlorothiophenolate ion is lower than that of the parent thiophenol. The other by-product, HCl, is formed as a gas and its formation does not affect the effectiveness or the catalytic activity of the clay which is evident from similar results observed when the clay is reused. The same reaction is also carried out in ethanol medium as well as at room temperature (details are given in table 1). Though similar products are obtained in both cases, the reaction is slower at room temperature. When a blank experiment (just mixing the two reagents without Cat-1) is carried out, there is no reaction.



R = C₆H₅, *p*-MeOC₆H₄, *p*-ClC₆H₄, C₄H₉, C₆H₁₃, C₈H₁₇

X = H, NO₂, MeO

Scheme 1.

Table 1. Reaction conditions and percentage yields of (HPLC) sulphides ArCH₂SR (1) in the reaction between RSH and ArCH₂Cl in clay-3-APTES composite at 95°C.

No.	R	Ar	Time	Yield of 1 in			Ref.
				KSF	K10	Bentonite	
1a	Ph	Ph	5 min	75	82	67	8a
1b	<i>p</i> -MeOC ₆ H ₄	Ph	12 h	12	12	5	8a
1c	<i>p</i> -ClC ₆ H ₄	Ph	30 min	83	99	89	8b
1d	Me(CH ₂) ₃	Ph	2.5 h	77	89	75	8c
1e	Me(CH ₂) ₅	Ph	8 h	84	92	89	8c
1f	Me(CH ₂) ₇	Ph	10 h	69	90	90	8d
		Ph	2 h ^a	12	11	11	
		Ph	15 min ^b	64	60	60	
		Ph	90 min ^c	49	50	48	
		Ph	2 h ^d	–	–	–	
		Ph	90 min ^c	60	60	62	
1g	Ph	<i>p</i> -NitroPh	4 h	40	50	41	8e
1h	<i>p</i> -MeOC ₆ H ₄	<i>p</i> -NitroPh	20 h	2	2	–	8f
1i	<i>p</i> -ClC ₆ H ₄	<i>p</i> -NitroPh	8 h	41	52	39	8g
1j	Me(CH ₂) ₃	<i>p</i> -NitroPh	12 h	2	2	2	8g
1k	Me(CH ₂) ₅	<i>p</i> -NitroPh	15 h	8	8	7	8g
1l	Me(CH ₂) ₇	<i>p</i> -NitroPh	16 h	8	9	7	8g
1m	Ph	<i>o</i> -NitroPh	4 h	53	52	43	8h
1n	<i>p</i> -MeOC ₆ H ₄	<i>o</i> -NitroPh	20 h	2	2	1	–
1o	<i>p</i> -ClC ₆ H ₄	<i>o</i> -NitroPh	8 h	49	62	47	–
1p	Me(CH ₂) ₃	<i>o</i> -NitroPh	12 h	2	2	1	8g
1q	Me(CH ₂) ₅	<i>o</i> -NitroPh	15 h	8	8	8	8g
1r	Me(CH ₂) ₇	<i>o</i> -NitroPh	16 h	7	9	7	8g
1s	Ph	<i>p</i> -MeOPh	5 min	75	99	92	8i
1t	<i>p</i> -MeOC ₆ H ₄	<i>p</i> -MeOPh	12 h	20	25	18	8j
1u	<i>p</i> -ClC ₆ H ₄	<i>p</i> -MeOPh	20 min	96	99	98	8k
1v	Me(CH ₂) ₃	<i>p</i> -MeOPh	1-30 h	45	49	50	8k
1w	Me(CH ₂) ₅	<i>p</i> -MeOPh	5-20 h	50	63	59	8l
1x	Me(CH ₂) ₇	<i>p</i> -MeOPh	10 h	92	93	90	8d

^aAt room temperature; ^breaction in 50 ml EtOH in presence of basic clay; ^cin 0.3 mol dm⁻³ of 0.3 ml of 3-APTES without clay; ^dblank experiment (without solvent and catalyst, i.e. just mixing two reagents); ^ein homogeneous media, stirring for 90 min and then reflux in a steambath with NaOEt for 2 h (reported⁷ procedure—in the absence of clay)

In the case of aliphatic thiols, the yield of the reaction decreases with increase in the length of the alkyl chain. This may be due to the difficulty experienced by long chain thiols in entering the clay interlayer and it can also be attributed to the increase in electron-releasing capacity with increasing chain length. In general, compared to aromatic thiols, aliphatic thiols take more time for completion of the reaction.

In addition to different type of thiols, we have also employed different substituted benzyl chlorides containing electron-withdrawing (*p*-nitro, *o*-nitro) and electron-releasing (*p*-methoxy) groups. In the case of substituted benzyl chlorides with electron-withdrawing substituents, reaction rate is slow compared to the parent compound. In those with electron-releasing substituents, reaction is very fast. This observation prompted us to propose that the reaction is more S_N1-like, since an opposite effect or no simple correlation of substituents would be observed if the reaction were S_N2. Further support for

an S_N1 -like reaction under the given set of conditions can be obtained from the readiness with which benzyl halides undergo facile polymerisation with acidic clays. This demonstrates the significant role that can be played by the clay microenvironment in generating and stabilising cationic intermediates. This reaction is also studied in KSF-montmorillonite-3-APTES and bentonite-3-APTES catalysts. Similar results are observed in these two cases. The reaction conditions and percentage of sulphides formed are shown in table 1.

The studies are also extended to the reaction of dithiols (1,3-propanedithiol and 3,4-toluenedithiol) with different types of benzyl chlorides (taken in 1:1 ratio). With

Table 2. Percentage conversion and products yield (HPLC) in the reaction between 3,4-toluenedithiol and substituted benzyl chlorides ($ArCH_2Cl$) in modified clays^a.

Ar	Percentage conversion	Yield (%) of		
		(2)	(3)	Unidentified products
Ph	88	36	30	22
Ph	— ^b	—	—	—
Ph	48 ^c	6	1	41
Ph	98 ^d	22	47	29
Ph	86 ^e	30	30	26
Ph	86 ^f	35	35	16
<i>p</i> -MeOPh	100	7	70	6
<i>p</i> -NitroPh	10 ^g	4	1	5
<i>o</i> -NitroPh	15 ^g	12	1	2

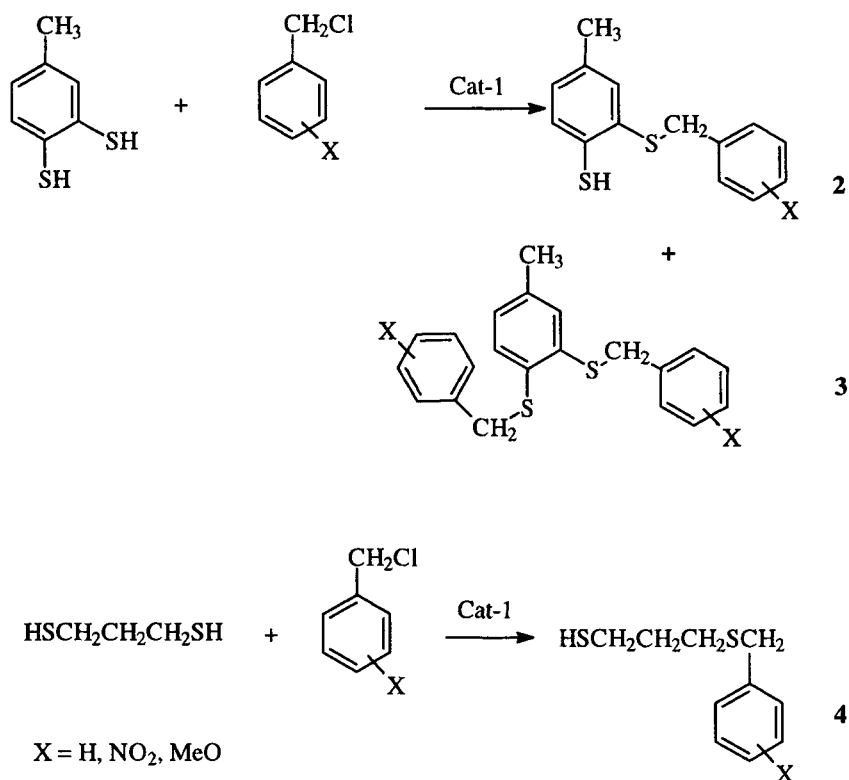
^aReaction in K10-montmorillonite-3-APTES for 45 min (heated in water bath); ^bblank experiment; ^creaction in 0.5 ml of 0.33 mol dm⁻³ of 3-APTES for 45 min; ^dreaction in C₂H₅ONa for 45 min; ^ereaction in KSF-montmorillonite-3-APTES 45 min; ^freaction in bentonite-3-APTES for 45 min; ^greaction time for nitrosubstituted benzyl chlorides is 6 h

Table 3. Percentage conversion and products yield (HPLC) in the reaction between 1,3-propanedithiol and substituted benzyl chlorides ($ArCH_2Cl$) in modified clays^a.

Ar	Percentage conversion	Yield (%) of	
		(4)	Unidentified products
Ph	— ^b	—	—
Ph	56 ^c	—	56
Ph	100 ^d	32	68
Ph	100 ^e	13	87
Ph	100	72	28
Ph	86 ^f	48	28
Ph	84 ^g	54	30
<i>p</i> -MeOPh	97	30	67
<i>p</i> -NitroPh	45 ^h	22	23
<i>o</i> -NitroPh	14 ^h	3	11

^aReaction in K10-montmorillonite-3-APTES for 45 min; ^bblank experiment; ^creaction in 0.33 mol dm⁻³ of 0.5ml of 3-APTES in 5 ml of absolute alcohol for 45 min; ^dreaction in C₂H₅ONa for 45 min; ^ereaction in natural clay; ^freaction in KSF-montmorillonite-3-APTES; ^greaction in bentonite-3-APTES; ^hreaction time with nitrosubstituted benzyl chloride is 6 h

substituted benzyl chlorides also, a similar trend in reactivity has been observed. However, in the case of 1,3-propanedithiol, only one thiol group reacts with benzyl chloride to give (4) but in the case of 3,4-toluenedithiol, both the thiol groups are affected thus resulting in both monobenzylated (2) as well as dibenzylated sulphides (3) (in the case of 3,4-toluenedithiol, in table 2, the remaining unreacted material is only 3,4-toluenedithiol). The results are presented in tables 2 and 3 and the reaction sequence is shown in scheme 2.



Scheme 2.

In the case of 3,4-toluenedithiol, after monobenylation, removal of the second proton from thiol, is facilitated by the stronger $-I$ effect of the benzylated first S atom and this effect is transmitted much more efficiently through two aromatic carbons (sp^2) which separates the two S atoms. However, in the case of the 1,3-propanedithiol, this $-I$ effect is less significant as now the two S atoms are separated by a three-carbon chain (aliphatic sp^3). Thus, while 3,4-toluenedithiol undergoes efficient dibenylation, in the case of 1,3-propanedithiol, monobenylation is the major course of the reaction.

Thus, reactions between substituted benzyl chlorides and thiols, studied for the first time in heterogeneous media, mainly depend on (i) basicity of modified clay (improved by the ethoxy/amino groups), i.e. the ability to remove protons from the corresponding thiols, (ii) nucleophilicity of the thiophenolate ions, and (iii) substitution in benzyl chloride. These studies also indicate that the clay-catalysed reaction (nucleophilic

substitution at a benzylic centre) is superior to reaction in a homogeneous medium because the organised aluminosilicate layer leads to quantitative conversion to products. The reaction is very convenient to carry out since the catalyst can be easily filtered off and may be reused.

Acknowledgements

Financial assistance provided by the Council of Scientific and Industrial Research, New Delhi is gratefully acknowledged. The authors thank Professors C Srinivasan and S Rajagopal for valuable suggestions.

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