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Clay-catalysed radical addition of aliphatic thiols to styrene

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When placed in K10-montmorillonite and cation-exchanged clays, alkanethiols undergo facile anti-Markovnikov addition to styrene by way of a radical mechanism forming sulfides. Surfactant pillared clays are found to be remarkably selective by suppressing side reactions.

Keywords: montmorillonite clay, catalysis, anti-Markovnikov addition, CTAC pillared clays, selectivity

1. Introduction

Cation-exchanged montmorillonites, pillared clays and clay-supported reagents [1–6] find extensive applications in organic synthesis under milder conditions. Unlike other conventional catalysts, these modified clays enjoy considerable advantages such as easier handling, regeneration, low cost, facile modification of acidity by suitable exchange of cations and elimination of metal waste like aluminium. Our interest in modified clays and also our recent report on sulfide synthesis using a modified basic clay [6], prompted us to undertake other routes for sulfide synthesis by employing clays as viable media.

An earlier work reported [1a] the addition of hex-1-ene with butane-1-thiol at 210°C to give hex-1-yl but-1-yl sulfide (1-isomer) in 12% yield by way of an anti-Markovnikov addition. The 2- and 3-isomers were also formed in 30 and 23% yield (Markovnikov addition). At low temperature, the 1-isomer was the major product. When the temperature was raised, the yield of 2- and 3-isomers increased and that of the 1-isomer decreased. The formation of the 1-isomer was proposed to involve free radical intermediates. H_2S addition of olefins in the presence of acid-impregnated clays to yield sulfides was also reported [7]. However, the mechanistic details and also the role of the clay mineral are not well defined. This prompted us to study the addition of thiols (butanethiol, hexanethiol and octanethiol) to an aryl olefin, namely styrene (which can generate a more stable radical intermediate in the proposed addition), with a view to gain an insight into the mechanism of addition and also the role of the clay interlayer.

2. Experimental

2.1. Reagents and catalysts

Thiols, styrene (Fluka) and K10-montmorillonite (Aldrich), were used as received. Cation-exchanged montmorillonite clays were prepared by standard procedure [6,8]. Surfactant-pillared clay was prepared by stirring sodium-exchanged clay (6 g) in 0.15 M solution of cetyltrimethylammonium chloride (CTAC) for 100 h at 53°C. The solution was filtered, washed repeatedly with distilled water and dried overnight in an oven. XRD data show that the spatial distance in the 001 plane increases from 9 to 16 Å and FT-IR spectra show characteristic stretching frequencies of long chain alkyl groups.

2.2. Addition procedure

To an equimolar mixture of thiol and styrene (0.008 M), 0.2 g of clay was added, mixed intimately and heated in a water bath (95°C) for 1 h. The reaction mixture was extracted with diethyl ether and dried over anhydrous sodium sulphate. After removing the solvent, the products were separated by column chromatography using hexane as the eluant. With CTAC-pillared clay, the reaction mixture was heated in an oil bath at 145°C for 1 h.

2.3. Analysis of the reaction mixture

The percentage conversion was obtained by analysing the reaction mixture in a Shimadzu LC-8A modular h.p.l.c. system (reverse phase column (ODS), UV-detector at 258 nm) using 70% methanol as the mobile phase and in each case the retention time for the starting material was taken as the internal reference. As the disulfides were not traced by h.p.l.c, the relative amounts of the different products were calculated from GC-MS (Hewlett-Packard 5590). The formation of alkyl 2-phenylethyl

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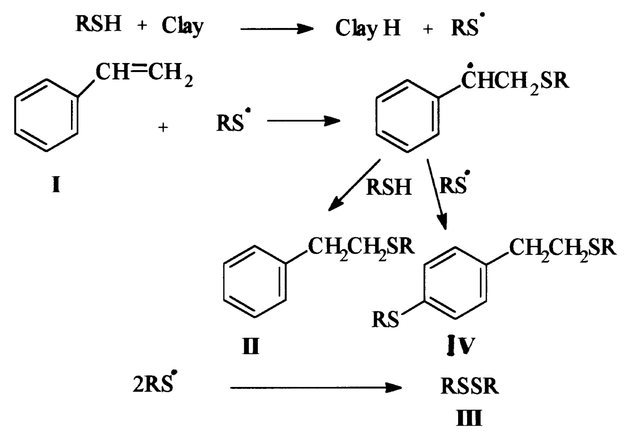

Scheme 1.

sulfide II as the product was confirmed from mass, NMR and IR spectral evidences and also by elemental analysis (anal. for $C_{14}H_{22}S$: calculated (%) C 75.67, H 9.90; found (%) C 75.42, H 9.97.). Products III and IV were identified from GC-MS. As their amount is lesser, it was not attempted to isolate and characterise them.

3. Results and discussion

In the proposed addition of thiols to styrene, in all the three cases, sulfide II formed by the anti-Markovnikov addition is obtained as the major product indicating only radical addition as the major route (scheme 1). Significant amounts of dialkyl disulfides III ($\sim$ 15%) and also IV ($\sim$ 20%), which is a mixture of isomeric products formed by the addition of two molecules of thiol to one molecule of styrene, are formed. The percentage conversion and the products distribution are presented in table 1.

The Markovnikov product (addition involving an ionic mechanism) is not formed with any of the thiols. The operation of a radical route is also evidenced by the observation of a very slow reaction in the case of H^+-exchanged clays, which are more suited for ionic additions. The significant decrease in reaction with H^+-exchanged clay is attributed to the more efficient protonation of styrene in this case (generating a carbonium ion of the type $C_6H_5\overset{+}{C}HCH_3$). This decreases the effective concentration of free styrene available for radical addition, which, we believe, must be faster under our experimental conditions. A blank experiment, in which

Table 1
Extent of conversion and product distribution in the addition of alkanethiols to styrene in the presence of clays [a]

Nature of clay	Conversion (%)	Percentage of products [b]		
		II	III	IV
	butanethiol			
K10-mont.	95	55	14	26
K10-mont.–H^+	45	25	07	13
K10-mont.–Al^{3+}	93	52	14	17
K10-mont.–Cr^{3+}	92	52	14	26
K10-mont.–Mn^{2+}	100	56	15	29
K10-mont.–Cu^{2+}	100	57	14	29
K10-CTAC [c]	59	59	–	–
	hexanethiol			
K10-mont.	78	45	13	20
K10-mont.–H^+	39	22	06	11
K10-mont.–Al^{3+}	66	38	10	18
K10-mont.–Cr^{3+}	80	46	13	21
K10-mont.–Mn^{2+}	89	51	15	13
K10-mont.–Cu^{2+}	100	57	17	26
K10-CTAC [c]	55	55	–	–
	octanethiol			
K10-mont.	74	55	09	10
K10-mont.–H^+	13	10	01	02
K10-mont.–Al^{3+}	60	45	07	08
K10-mont.–Cr^{3+}	60	46	07	07
K10-mont.–Mn^{2+}	75	56	08	11
K10-mont.–Cu^{2+}	100	74	12	14
K10-CTAC [c]	37	37	–	–

[a] In K10-montmorillonite and ion-exchanged clays, the reaction mixture is heated at 95°C for 1 h.
[b] Refer to scheme 1.
[c] An equimolar (8.68×10^{-3} M) ratio of thiol and styrene is heated with 0.2 g of pillared clay in an oil bath (145°C) for 1 h.

a mixture of thiol and styrene is heated to 95°C, does not yield any addition product. Thus the present work amply demonstrates the ability of the clay microenvironment to function as a radical initiator.

When a hydrophobically modified clay such as CTAC-pillared clay is employed, the formation of III and IV is totally suppressed and the sulfide II formed by anti-Markovnikov addition is the exclusive product. This remarkable directed addition of thiol to olefin may be rationalised by visualising both the hydrocarbon chain of thiol and the aryl ring of styrene embedded in the hydrophobic pillar, namely CTAC and the functional groups are oriented towards the ionic interface of the pillaring agent and the clay surface. It is also likely that the hydrocarbon pillars may have impeded the movement of radical intermediates.

A closer look at the data reveals that, on increasing the chain length of thiol, the percentage conversion decreases and also the side products III and IV are formed in lesser amounts. This may be attributed to the restricted diffusion of the radical fragments upon increasing the chain length. The sensitivity of thiyl radical addition to styrene towards steric effects is known and well documented [9].

4. Conclusions

The efficiency of K10- and cation-exchanged montmorillonite clays to act as radical initiators as well as the selectivity of CTAC-pillared clays in the addition of aliphatic thiols to styrene have been demonstrated in the present work. This specific anti-Markovnikov addition (in contrast to the normal acid-catalysed addition) provides an excellent route for the synthesis of asymmetrical sulfides.

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