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# Montmorillonite K 10-catalyzed regioselective addition of thiols and thiobenzoic acids onto olefins: an efficient synthesis of dithiocarboxylic esters

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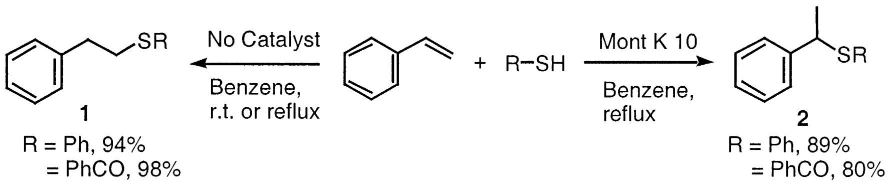
**Abstract**—The addition of thiols and thiobenzoic acids onto olefins proceeded regioselectively in a Markovnikov manner in the presence of Montmorillonite K 10 (Mont K 10) clay as the catalyst to afford thioethers and thiocarboxylic *S*-esters, while high selectivity to anti-Markovnikov products was realized in the absence of any catalyst. Treatment of the esters with Lawesson's reagent provided the corresponding dithiocarboxylic esters in high yields. © 2001 Elsevier Science Ltd. All rights reserved.

The addition of thiols onto carbon–carbon double bonds may proceed via an electrophilic pathway involving ionic processes or a free-radical-chain pathway.[1] The main emphasis in the literature has been on the free-radical pathway[2] and little work exists on the electrophilic pathway. The electrophilic addition of thiols is catalyzed by protic acids[3] ($H_2SO_4$, $HClO_4$ and *p*-TSA) and Lewis acids[4] ($AlCl_3$, $BF_3$, $TiCl_4$, $SnCl_4$, $ZnCl_2$, $SO_2$). Recently, it was reported that thiols add onto olefins in an anti-Markovnikov fashion in the presence of acidic H-Rho zeolite.[5] However, control experiments were not reported and, thus, the role of the zeolite catalyst when obtaining anti-Markovnikov products was not clearly defined. Although the Markovnikov addition of thiols onto carbon–carbon double bonds is well known, reactions onto styrenic substrates are noticeably rare, probably due to their facile polymerization under acidic conditions. Hence, it is of interest to develop new methods using catalysts with mild acidities to perform the addition reaction under truly heterogeneous conditions so the reactivity of thiols towards styrene and its derivatives can be moderated. Commercially available Mont K 10 clay is one such material that can fulfill these requirements. In addition, clays have many advantages, such as ease of handling, non-corrosiveness, low cost and regeneration. Clays function as efficient catalysts for various organic transformations due to their Brønsted and Lewis acidities in both their natural and ion-exchanged forms.[6] We became interested in the synthesis of dithiocarboxylic esters (**3**), which are used as chain-transfer agents for the synthesis of polymers with well-defined molecular architectures in living-radical polymerizations (reversible addition–fragmentation chain transfer, the RAFT process).[7,8] Several procedures for the synthesis of dithioesters are known in the literature including: (i) alkylation of dithioacid salts,[9] (ii) thiohydrolysis of imidothiolates,[10] (iii) oxidative sulfuration of benzyl halides,[11] (iv) transesterification of dithioesters with thiols,[12] exchange of bis(thiocarbonyl) disulfides with azo compounds[13] and condensation of thiols and alcohols with carboxylic acids in the presence of $P_4S_{10}$.[14,15] How-



**Scheme 1.**

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*Keywords*: addition reactions; alkenes; thiols; clays; sulfur compounds; chain-transfer agents; living-radical polymerization; reversible addition–fragmentation chain-transfer polymerization.

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ever, they suffer from drawbacks such as expensive reagents, use of basic conditions and incompatibility of reactive functional groups (e.g. $NO_2$, CN) under Grignard conditions. In this paper, we report the preparation of thiocarboxylic *S*-esters from olefins and thiobenzoic acids in the presence and absence of clay catalysts giving rise to Markovnikov and anti-Markovnikov addition products, respectively (Scheme 1).

Table 1 presents the results of the regioselective addition of thiophenol and thiobenzoic acid onto styrene both in the presence and absence of catalysts. For example, in the absence of any catalyst, the S–H addition takes place in an anti-Markovnikov fashion leading to the linear structure **1** in high yields. However, in the presence of Lewis acid-type catalysts, such as clays (e.g. $AlCl_3$, etc.), the S–H addition onto C=C proceeded in a Markovnikov manner giving branched structure **2** in high yields. A search of the literature revealed the lack of a systematic study carried out to establish the nature of the products resulting from the addition of thiophenol to olefins *in the absence of a catalyst*.[16]

Table 2 shows the results of the regioselective addition of thiophenol and thiobenzoic acid onto various olefins in the absence of any catalyst. All reactions were carried out in nitrogen using freshly distilled reagents to eliminate oxygen and peroxide impurities, respectively. Surprisingly, the addition of both thiophenol and thiobenzoic acid onto alkenes takes place in an anti-Markovnikov fashion leading to linear structures **1** either at 25 or 80°C with high conversions (>90%). To obtain more information on the nature of the intermediate, an experiment was carried out in the presence of galvinoxyl radical as a spin trap at 25°C under nitrogen. However, the addition reaction still proceeded to give a linear structure in high yields, thus eliminating the possibility of involvement of radical species. The formation of anti-Markovnikov products may be explained by presuming that the addition of S–H onto C=C bonds takes place in a concerted manner with steric factors controlling the regioselectivity.

Table 3 presents the results of the addition of various thiols and thiobenzoic acids onto a variety of olefins in the presence of Mont K 10 clay as the catalyst in refluxing benzene. Toluene was also used with equivalent results. Evidently, the addition of thiols or thioacids onto olefins in the presence of a clay catalyst proceeded largely in a Markovnikov fashion. However, in the case of aliphatic olefins (entries 12 and 13), considerable amounts of linear structures (30%) are formed. Also, poor selectivity to branched structures was observed in the case of 4-bromostyrene. Surprisingly, the addition of thiobenzoic acid onto methylmethacrylate in the absence or presence of acidic, basic or neutral clays gave, almost exclusively, anti-

**Table 1.** Regioselective addition of thiols/thioacids onto styrene[a]

| Entry | Thiols/thioacids | Catalyst | Conv. (%)[b] | Product distribution (%)[b] | | |
|---|---|---|---|---|---|---|
| | | | | **1** | **2** | Others[c] |
| 1 | Thiophenol | None | 95 | 97 | 2 | 1 |
| 2 | Thiophenol | Mont K 10 | 93 | 6 | 80[d] | 14 |
| 3 | Thiobenzoic acid | None | 100 | 98 | – | 2 |
| 4 | Thiobenzoic acid | Mont K 10 | 97 | 3 | 89 | 8 |
| 5 | Thiobenzoic acid | Mont KSF | 89 | 2 | 92 | 6 |
| 6 | Thiobenzoic acid | $AlCl_3$ | 96 | 5 | 95 | – |

[a] Styrene (10 mmol), thiol/thioacid (10 mmol), catalyst (10% wt), benzene (25 ml), 80°C, 24 h.

[b] Based on GC–MS analysis.

[c] Mixtures of product, uncharacterized.

[d] Identical results were obtained with recovered catalyst in a subsequent experiment.

**Table 2.** Addition of thiols/thioacids onto olefins in the absence of catalyst: formation of anti-Markovnikov products[a]

| Entry | Olefin | Thiols/thioacids | Temp. (°C) | Conv. (%)[b] | Product distribution (%)[b] | | |
|---|---|---|---|---|---|---|---|
| | | | | | **1** | **2** | Others[c] |
| 1 | Styrene | Thiophenol | 25 | 97 | 94 | 2 | 4 |
| 2 | Styrene | Thiophenol | 80[d] | 99 | 98 | 2 | – |
| 3 | Styrene | Thiobenzoic acid | 25 | 94 | 97 | – | 3 |
| 4 | Styrene | Thiobenzoic acid | 80[d] | 92 | 95 | 3 | 2 |
| 5 | 1-Hexene | Thiobenzoic acid | 25 | 93 | 80 | 5 | 15 |
| 6 | 4-Acetoxystyrene | Thiobenzoic acid | 25 | 91 | 85 | 5 | 10 |
| 7 | Methylmethacrylate | Thiobenzoic acid | 25 | 96 | 93 | 2 | 5 |

[a] Olefin (10 mmol), thiol/thioacid (10 mmol), benzene (25 ml), 24 h, $N_2$.

[b] Based on GC–MS analysis, major products were thoroughly characterized by IR, $^1H$ and $^{13}C$ NMR, and MS analyses.

[c] Mixtures of product, uncharacterized.

[d] 10 h.

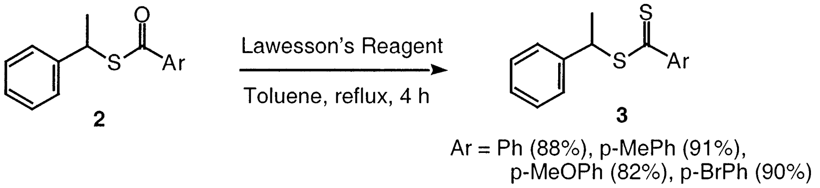
**Table 3.** Addition of thiols/thioacids onto olefins in the presence of Mont K 10: formation of Markovnikov products[a]

| Entry | Olefins | Thiols/thioacids | Conv. (%)[b] | Product distribution (%)[b] | | |
|---|---|---|---|---|---|---|
| | | | | **1** | **2** | Others[c] |
| 1 | Styrene | Thiophenol | 97 | 6 | 89 | 5 |
| 2 | Styrene | 2-Methylthiophenol | 22 | 5 | 91 | 4 |
| 3 | Styrene | *t*-Butylthiol | 74 | 31 | 59 | 10 |
| 4 | Styrene | Thiobenzoic acid | 93 | 6 | 80 | 14 |
| 5 | Styrene | 4-Methoxythiobenzoic acid | 96 | 25 | 65 | 10 |
| 6 | Styrene | 4-Bromothiobenzoic acid | 90 | 5 | 70 | 25 |
| 7 | 4-Methylstyrene | Thiobenzoic acid | 76 | 25 | 41 | 34 |
| 8 | 4-Methoxystyrene | Thiobenzoic acid | 38 | 2 | 83 | 15 |
| 9 | 4-Acetoxystyrene | Thiobenzoic acid | 62 | 13 | 72 | 15 |
| 10 | 4-Bromostyrene | Thiobenzoic acid | 23 | 13 | 12 | 75 |
| 11 | α-Methylstyrene | Thiobenzoic acid | 80 | 8 | 76 | 16 |
| 12 | 1-Hexene | Thiobenzoic acid | 85 | 30 | 61 | 9 |
| 13 | 1-Octene | Thiobenzoic acid | 76 | 30 | 62 | 8 |

[a] Olefin (10 mmol), thiol/thioacid (10 mmol), Mont K 10 (10% wt), benzene (25 ml), 80°C, 12 h.

[b] Analyzed by GC–MS, major products were thoroughly characterized by IR, $^1$H and $^{13}$C NMR, and MS analyses.

[c] Mixtures of product, uncharacterized.



**Scheme 2.**

Markovnikov product. The formation of Markovnikov products can be explained by an initial activation of the olefins by Lewis acid sites present in the clay catalysts that generates the more stable benzylic carbocations. Subsequent attack of the sulfur nucleophile results in the formation of branched structures **2**.

Finally, the reaction of thiol esters **2** with Lawesson's reagent in refluxing toluene affords the dithiocarboxylic esters **3** in excellent purified yields (Scheme 2).

For the highly hindered thiocarboxylic esters, such as that obtained from α-methylstyrene and thiobenzoic acid (entry 11, Table 3), harsher conditions (dry xylene, 150°C, 48 h) resulted in an 82% yield (by GC–MS) of the corresponding dithiocarboxylic ester, which, upon purification by column chromatography (neutral alumina, eluting with 1:1 benzene:chloroform), gave 62% isolated yield.

In summary, we have shown that the addition of S–H onto C=C bonds takes place regioselectively giving branched or linear structures depending upon the presence or absence of a Lewis acid catalyst. Subsequent treatment of the thiocarboxylic *S*-esters with Lawesson's reagent provides a new, simple and efficient method for the preparation of branched or linear dithiocarboxylic esters **3** in high yields.

## Typical experimental procedure

To a mixture of styrene (2.08 g, 0.02 mol) and Montmorillonite K 10 (208 mg, 10% wt) in benzene (40 ml) was added thiobenzoic acid (2.76 g, 0.02 mol). The mixture was refluxed for 12 h, cooled and the solid catalyst was removed by filtration. Distillation of benzene gave the crude product, which was further purified by column chromatography (neutral $Al_2O_3$, eluting with toluene). The purity of the monothioester was found to be >99% (GC–MS). Isolated yield: 3.72 g, 77%.

A mixture of the monothioester (2.42 g, 0.01 mol) synthesized above and Lawesson's reagent (2.02 g, 0.005 mol) in toluene (40 ml) was refluxed for 3 h. The progress of the reaction was monitored by GC–MS. After the reaction was complete, it was cooled and the product purified by passing it through a column packed with neutral $Al_2O_3$ and eluting with toluene. Distillation of toluene gave dithioester (99.2% purity by GC–MS). Yield: 2.27 g, 88%.

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