Montmorillonite-catalysed addition of alkyl disulfides to alkenes

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A mild method for 1,2-addition of alkyl disulfides to alkenes and conjugated polyenes catalysed by MCl_x-promoted montmorillonite clays is reported. Alkenes undergo 1,2-trans addition affording MCl_x-complexed derivatives, which are readily converted to alkylthio-derivatives on reaction with EDTA. Conjugated polyenes yield 1,2-trans addition and 1,*n*-addition products, with 1,2-addition compounds being found at low reaction temperatures.

Keywords: clayzic, dimethyl disulfide, alkenes, thioalkylation and disulfides

1. Introduction

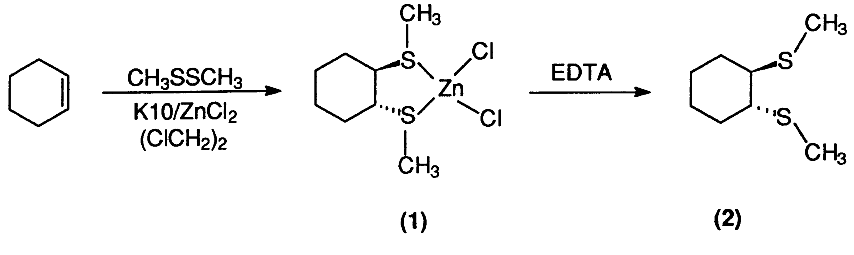
Only a few methods are available for the addition of alkyl disulfides to double bonds [1–8]. One of the best studied methods uses BF_3–OMe_2 catalysed addition of dimethyl disulfide (DMDS) [6]. These conditions promote trans-addition to alkenes but result in poor yields using other disulfides or for addition of DMDS to conjugated dienes. Disulfide addition has also been accomplished using I_2, PhIO–TfOH, HF and $(CH_3S)_2Al(CH_3)$ but these reagents do not appear to have been used extensively [1–5,7,8].

Recently, we have described the use of metal-salt-promoted mesoporous montmorillonite clays to promote direct introduction of –SMe groups into thiophenes and benzothiophenes, using the ability of the catalyst to produce electrophilic sulfur by interaction of the disulfide with Lewis sites on the clay surface [9]. In this report, we describe the application of these catalysts for the facile trans-addition of DMDS and other disulfides to alkenes and the 1,2-addition of a disulfide to conjugated cyclodienes.

2. Results and discussion

Stirring a mixture of cyclohexene (1 mol equiv), DMDS (1.25 mol equiv) and K-10 montmorillonite in 1,2-dichloroethane at 20°C resulted in the formation of **2**, (50%) after 8 h (scheme 1). No reaction was observed with free $ZnCl_2$. However, use of K-10 impregnated with $ZnCl_2$ (2 mmol $ZnCl_2$ per gram of K-10) gave a clean and rapid conversion (2–3 h) to the trans-addition product (**1**) (table 1) complexed to $ZnCl_2$. This complex, which was isolated by trituration of the crude product with hexane, has been characterized fully by single-crystal X-ray analysis [10]. The uncomplexed product (**2**) was obtained in 87% yield by treatment of the crude reaction product with a solution of EDTA in acetone/H_2O (1 : 1). Thus, K-10/$ZnCl_2$ appears to be a very efficient catalyst for the addition of DMDS to cyclohexene in comparison to either K-10 or free $ZnCl_2$, but the product **2** readily coordinates to $ZnCl_2$ removing it from the clay surface as **1**. The X-ray analysis shows, unequivocally, that $ZnCl_2$ is not consumed in promoting C–S bond formation, but is chelated by the product.

In experiments where a sub-stoichiometric quantity of $ZnCl_2$ (impregnated on K-10) was used, a mixture of the free adduct (**2**) and the $ZnCl_2$-complex was obtained. This observation suggests that the adduct (**2**) does not



Scheme 1.

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Table 1
Reaction of DMDS with cyclohexene in the presence of metal-salt-impregnated K-10

Catalyst type	Yields		Total yield of **2** [a] (%)
	1	**2**	
K-10/$ZnCl_2$	80	0	87
K-10/$CuCl_2$	51	13	60
K-10/$FeCl_2$	48	17	63
K-10/$FeCl_3$	32	45	75

[a] Purified by a Kuglerohr distillation after treatment with EDTA.

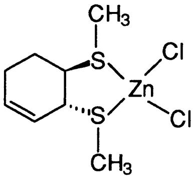
always remove $ZnCl_2$ from the surface. Addition of DMDS to cyclohexene was also facilitated by catalysts comprising of K-10 impregnated with either $CuCl_2$, $FeCl_2$ or $FeCl_3$ (table 1). In each case, the product was obtained as a metal complex from which the free adduct could be obtained by treatment with EDTA. This observation is interesting in that it shows that K-10/$ZnCl_2$ and related catalysts consist of clay surfaces with $ZnCl_2$, $CuCl_2$, $FeCl_2$ or $FeCl_3$ located within the mesopores of the clay structure and not the oxidic forms as might be expected as a result of calcination procedures utilized during catalyst preparation [11].

Addition of DMDS to hex-1- and 2-ene also proceeded smoothly in the presence of K-10/$ZnCl_2$ yielding the trans-products as $ZnCl_2$-complexes in each case. Despite the limited free space within the mesopores of K-10 (20–80 Å), heptadec-1-ene also gave a respectable yield (61%) of a $ZnCl_2$-complexed trans-addition product after 2 h at 20°C. Removal of uncomplexed sulfide products and any organic impurities was accomplished by washing the crude product with hexane.

Reaction of 1,3-cyclohexadiene with DMDS at 20°C resulted in an excellent yield (>75%) of a 1 : 1 mixture of the trans-1,2- and 1,4-adducts. Purification of the trans-1,2-adduct was facilitated by the formation of the metal complex such that trituration with hexane removed the more soluble 1,4-adduct from the 1,2–metal complex. By reducing the reaction temperature to −30°C, the 1,2-compound could be obtained as the major product (70 : 30 1,2- versus 1,4-addition). It was not possible to deduce from ^{1}H NMR spectra whether the 1,2-addition had occurred cis or trans. However, single-crystal X-ray analysis of the $ZnCl_2$ complex showed that trans-addition had taken place [12]. Thus, formation of the 1,2-adduct most likely takes place via an intermediate episulfonium salt in a mechanism similar to that proposed by Caserio et al. [6] for BF_3–OMe_2-catalysed addition of DMDS to alkenes (scheme 2).

Unexpectedly the reaction of cycloheptatriene and DMDS at −30°C, yields the cis-$ZnCl_2$-complex (**4**) from a K10/$ZnCl_2$-catalysed reaction although in relatively low isolated yield (21%).

Since cis-addition has not been observed previously for additions of disulfides to alkenes or polyenes, its structure was confirmed by single-crystal X-ray analysis [12].



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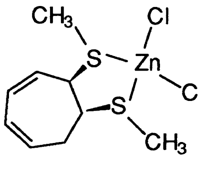
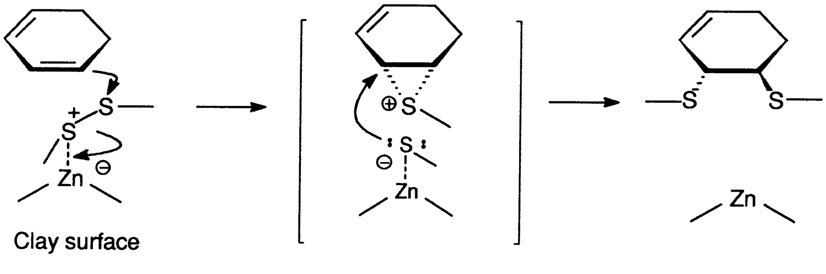


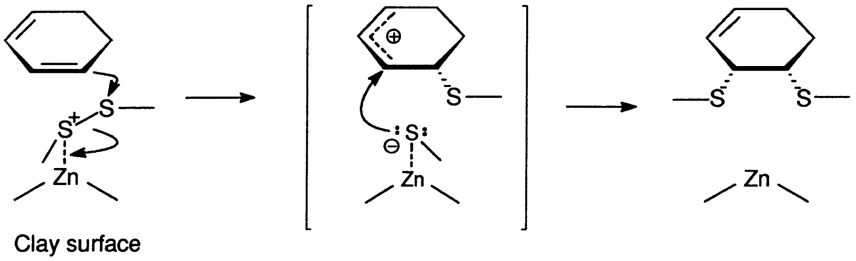
(4)

Formation of the cis-product is most readily explained through attack of MeS^- on a resonance-stabilized carbocation intermediate (scheme 3). Both cis- and trans-products might be expected to arise from such an intermediate, although to date, perhaps due to the generally poor nature of the reaction, we have not been able to isolate the trans-adduct from reaction of DMDS with cycloheptatriene catalysed by K-10/$ZnCl_2$.

Other dialkyl disulfides (ethyl, *n*-propyl, *n*-butyl) were employed with moderate success. It was found that the larger the alkyl chain on the disulfide the longer the reaction times became, with isolated yields of all reactions at about 50%. In all cases, clay catalysts removed from these reactions can be recycled after re-impregnation of the metal salt phase. Overall, the clay-catalysed addition of DMDS and other disulfides to alkenes is of significant interest as it affords a simple preparation for 1,2-thioalkyl compounds using a readily available catalyst and illustrates the nature of the active species in clayzic (K-10/$ZnCl_2$) catalysts. In addition, unlike the BF_3–OEt_2 system, K-10/$ZnCl_2$ catalysts promoted reaction with ethyl, *n*-propyl and *n*-butyl disulfides.



Scheme 2.



Scheme 3.

Further studies in our laboratories are examining the synthetic utility of 1,*n*-addition of disulfides and thiols to electron-rich systems.

3. Experimental

K-10/ZnCl$_2$ (clayzic) catalyst preparation. K-10 montmorillonite (Fluka Chemical Company, used as received) was modified by addition of $ZnCl_2$ (2 mmol per gram of clay) using wet impregnation procedures described previously [9,11]. The modified catalyst was activated by heating at 150°C for 24 h and was stored in a desiccator. Cu and Fe-based catalysts are prepared by the same method using $CuCl_2$, $FeCl_2$ and $FeCl_3$. Surface areas and mesopore volumes of these catalysts fall in the range 130 $m^2\ g^{-1}$ and 0.30 $ml\ g^{-1}$ respectively.

General synthesis of 1,2-bis(thiomethyl)alkyl zinc chloride compounds. Clayzic or other K-10 metal salts catalysts (25 g) were suspended in a solution of 1,2-dichloroethane (60 ml) and dimethyl disulfide (30 mmol) by vigorous stirring. A solution of an alkene (25 mmol) in 1,2-dichloroethane (10 ml) was added dropwise to the mixture. After 2 h, acetonitrile (10 ml) was added to the reaction mixture and the solution was stirred for another 5 min. The solution was filtered and the solvent was evaporated giving either viscous oils or solids. These products were washed with hexane (2×30 ml) and purified by crystallization or distillation.

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