

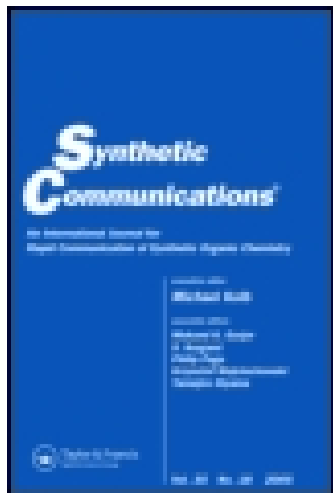
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### Montmorillonite KSF, a Mild and Efficient Catalyst for Benzodithiepination of Carbonyl Compounds

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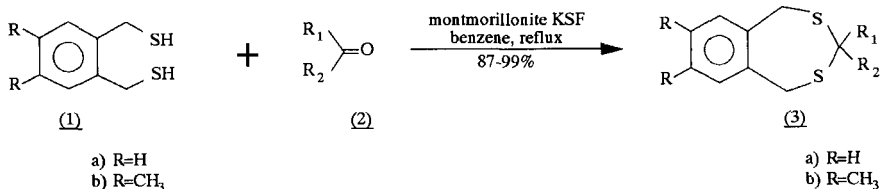
**MONTMORILLONITE KSF, A MILD AND EFFICIENT CATALYST FOR BENZODITHIEPINATION OF CARBONYL COMPOUNDS**

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**Abstract:** A mild and efficient procedure for the protection of carbonyl compounds as 1,5-dihydro-3H-2,4-benzodithiepinines in high yields is described by using a readily available and inexpensive KSF clay catalyst.

1,3-Dithiolanes have long been used as protective groups for carbonyl compounds<sup>1,2</sup> and as synthons in a variety of synthetic operations<sup>3</sup>. The preparation of these dithiolanes employs thiol or dithiol reagents which generally have unpleasant odours, as do the products. To overcome this problem Shahak et al<sup>4</sup> used 1,2-dimethyl-4,5-benzenedimethanethiol (**1b**) which forms highly crystalline benzodithiepinines (**3b**) with hardly any odour. The catalysts employed in this work were strong protic acids such as concd HCl (aq) for aldehydes, ZnCl<sub>2</sub>-HCl (g) or concd H<sub>2</sub>SO<sub>4</sub> for ketones.



We recently reported a high yielding method for the preparation of 2,4-benzodithiepinines (3a) using a more readily available reagent 1,2-benzenedimethanethiol (1a) and employing anhyd. iron (III) chloride-silica gel as mild catalyst<sup>5</sup>. We now wish to report that KSF clay, an acidic montmorillonite type phyllosilicate<sup>6-14</sup> (Hammett acidity  $H_o \sim -7$ ) is an extremely efficient catalyst for the condensation of carbonyl compound with 1,2-benzenedimethanethiol (1a) under mild conditions. The present method is even more convenient, as it eliminates the need for catalyst preparation, since KSF is inexpensive and readily available. Both reaction conditions and work-up procedure are very simple and convenient. When a mixture of carbonyl compound (1a) and KSF clay is heated and stirred under reflux, with water removed azeotropically, excellent yields of benzodithiepinines (3a) are obtained (87-99%, see Table). The superiority of using KSF clay is clearly manifested in that the less reactive aromatic ketones also converted to corresponding (3a) in high yields (Table, Entries 12-14). The reaction proceeds very cleanly and the product isolation is achieved by mere filtration and evaporation.

In conclusion, commercially available and inexpensive clay catalyst is very effective in benzodithiepination of a variety of carbonyl compounds (including the aromatic ketones) under mild reaction conditions. This method should provide a useful alternative to the currently used thioacetalization as the products formed are crystalline solids, have mild odour and the blocking group is easily removable.

### **Benzodithiepination of Carbonyl Compounds**

**General Procedure:** To a stirred solution of 1,2-benzenedimethanethiol<sup>5</sup>

**Table: Benzodithiepination of Carbonyl Compounds using Montmorillonite KSF**

Entry	Substrate	Benzodithiepinines (3a) a,b(% yield)	Substr <sup>c</sup> ratio	Rxn Time (h)
1	Cyclohexanecarboxaldehyde	96	1.5	1.5
2	Phenylacetaldehyde	88	1.5	2
3	Benzaldehyde	99	1.2	1.5
4	p-Chlorobenzaldehyde	91	1.0	3
5	Anisaldehyde	99	1.2	1.5
6	Cinnamaldehyde	98	1.2	4
7	Cyclohexanone	92	1.5	8
8	Cyclopentanone	94	1.5	17
9	2-Methylcyclohexanone	91	1.2	17
10	3-Pentanone	87	2.0	8
11	2-Adamantanone	98	1.0	5
12	Acetophenone	88 <sup>d</sup>	1.2	12
13	9-Fluorenone	99 <sup>d</sup>	1.0	16
14	Benzophenone	99 <sup>d</sup>	1.0	40
15	Trioxane <sup>e</sup>	99 <sup>d</sup>	2.0	1.5

a) All products characterised by physical and spectral data; b) Yield refers to isolated pure product; c) (Carbonyl compound)/(1); d) 1.0g of clay KSF used; e) Source of formaldehyde .

(5mmol) and carbonyl compound (5-10mmole, see Table) in benzene (25ml) was added clay KSF<sup>15</sup> (500mg) (unless stated otherwise). The mixture was stirred and heated under reflux using a Dean-Stark apparatus for water separation. The progress of the reaction was monitored by IR and NMR spectroscopy. Upon completion of the reaction, the clay was filtered off, the solvent removed under vacuum and the crude product purified by recrystallisation (acetone-ethanol).

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