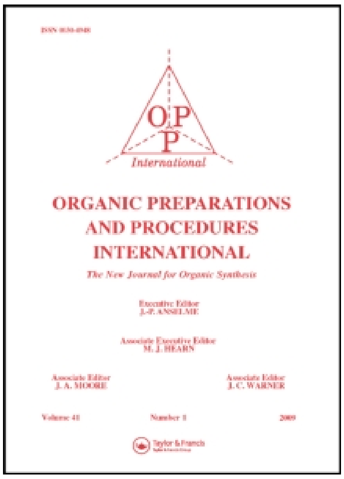

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# AN IMPROVED PROCEDURE FOR THE PREPARATION OF 1,3-DITHIANE

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# AN IMPROVED PROCEDURE FOR THE PREPARATION OF 1,3-DITHIANE

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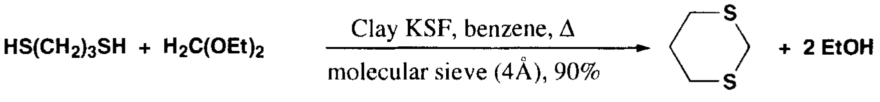
1,3-Dithiane has long been a valuable synthon in a variety of synthetic operations.[1-3] Since the pioneering work of Corey and Seebach[4] in 1965, the 1,3-dithiane moiety has been introduced by thioacetalization of a carbonyl group, using Lewis acid or acidic catalysts.[1] Although numerous methods have been reported for the preparation of 1,3-dithianes, generally not many describe specifically the preparation of 1,3-dithiane. The best known procedure for its preparation to date seems to be that initially reported by Corey and Seebach[5] and involves reacting 1,3-propanedithiol with methylal in the presence of boron trifluoride etherate-glacial acetic acid. However, this method requires special care in the addition of reactants (*viz.* 1,3-propanedithiol, methylal) over an 8 hrs period and special precautions to avoid side-reactions.[5] We report here an improved procedure for the preparation of 1,3-dithiane by condensation of 1,3-propanedithiol with ethylal in the presence of montmorillonite KSF clay catalyst. The reaction is carried out simply by heating (with magnetic stirring) a mixture of ethylal, 1,3-propanedithiol, benzene and KSF clay in the presence of 4Å molecular sieve at reflux. The reaction is catalyzed by the KSF clay, an acidic montmorrillonite type phyllosilicate[6] and driven to completion (8 hrs) by the removal of ethanol with molecular sieve.



The reaction proceeds very cleanly and the isolation of the product is very simple. The molecular sieve can be reactivated (350° overnight) and reused without affecting the yield significantly.

## EXPERIMENTAL SECTION

Melting points are uncorrected and were recorded on an electrothermal melting point apparatus. The $^1$H NMR spectra were recorded on a JEOL PMX-60 spectrometer with TMS as the internal standard. The chemicals, 1,3-propanedithiol, ethylal and montmorillonite clay KSF were purchased from Fluka chemicals and molecular sieve (4Å) from Union Carbide.

**1,3-Dithiane.** - To a two-necked 500 mL Erlenmeyer flask with ground-glass fittings was placed a mixture of 1,3-propanedithiol (16.8g, 0.15 mole), ethylal (18.1g, 0.165 mole), dry benzene (225 mL) and clay KSF (15g). The mixture was refluxed with magnetic stirring using a Soxhlet extractor containing a "Linde" type 4Å molecular sieve (180 g); half of the benzene used was poured through the molecular sieve contained in the Soxhlet in order to wet them. The progress of reaction was followed by $^1H$ NMR spectroscopy and was complete in 8 hrs. Upon cooling, the molecular sieves were washed with petroleum ether (40-60°) and the clay was filtered off. The organic layer washed successively with 1M NaOH (75 mL), water (75 mL), saturated NaCl (75 mL), dried ($Na_2SO_4$) and evaporated on a rotary evaporator (~30 mm pressure and 25° water-bath). The white-solid obtained was recrystallized from hot methanol to give 1,3-dithiane (14.2g) as a first fraction and a further 1.90g of product was obtained as a second fraction from the mother liquor. The total yield of 1,3-dithiane obtained was 16.1 g (90%), mp. 52-53°, lit.[5] 53-54°. $^1H$ NMR ($CDCl_3$): $\delta$ 2.05 (m, 2H), 2.82 (m, 4H), 3.75 (s, 2H).

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