A FACILE METHOD TO OBTAIN OXATHIOLANES BY BENTONITIC EARTH (TAAF) CATALYST

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Abstract: Treatment of carbonyl substrates with 2-mercaptoethanol in the presence of Tonsil Actisil FF (TAAF) as the catalyst, affords the corresponding oxathiolanes. Reaction yields are good and the work-up is very simple.

INTRODUCTION.

Several oxathiolanes have been studied recently in great detail as potent anti-HIV agents(1), some of them are useful as antiinflamatories (2), others exhibit bactericidal (1-4), fungicidal (5), antimuscarinidal (6), herbicidal and fitocidal (7), activities. In addition, they are also important because of its protective carbonyl group application.

Although, there are general methods described so far for the preparation of oxathiolanes involving different reagents, the most common synthetic methods used to obtain these compounds involves the presence of an Lewis acid catalyst, *eg* $ZnCl_2$, $BF_3{\cdot}Et_2O$, $AlCl_3$, $SnCl_2$ (8); those catalyst however, have severe restriction due to their higher cost (9). Moreover, the product yield and the success of the oxathiolanes depends largely upon the choice of catalyst and the reaction conditions, in this view the use of natural and modified clays as the catalytic promoter, represents an important and attractive alternative

Related with our research program (10) on the use of TAFF, a commercial smectite, this work deals with the results of experiments performed to obtain several oxathiolanes **1-7** using the clay of our interest as the catalytic moiety.

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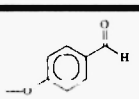
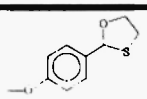
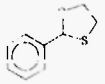
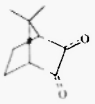
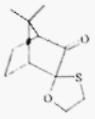
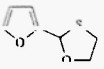
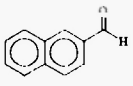
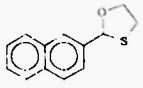
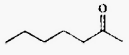
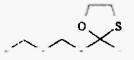
Table.-Condensation of carbonyl compounds and 2-mercapto ethanol promoted by TAFF.

	Substrate	Product	Yield (%)[a]
1			30
2			60
3			47
4			75
5			70
6			40
7			30

a) Yields are of isolated pure products; reaction time 3h on each entrie.

EXPERIMENTAL

Purified products were characterized by spectroscopic means: ^1H NMR spectra were recorded in a Varian FT-200 spectrometer using $CDCl_3$ as solvent and TMS as internal reference; EIMS (70 ev) spectra were obtained using a HP5985 B mass spectrometer. The natural clay was originally obtained from Tonsil Mexicana (9) and analyzed prior to use with a Siemens D-500 X-Ray Difractometer using the Cu K α_1 radiation; the Lewis acid character of clay was confirmed a Perkin-Elmer 1600 series FTIR spectrometer, using the pyridine coordination method[11].

General method.- 1,3-Oxathiolanes: A mixture of 10 mmol of carbonyl substrates and 2-mercapto ethanol (10 % molar in excess) in 40 ml of anhydrous benzene was allowed to reflux under stirring in presence of activated bentonite, employing a Dean-Stark trap, for approximately 3 h. The reaction was monitored by *tlc* (*n*-hexane/EtOAc 6:4), the reaction mixture was filtered over celite and the solution washed with acetone; then the solvent was removed under vacuum and the residue purified by column chromatography. Finally the products were characterized by (NMR and EIMS).

DISCUSSION

The results of several experiment performed with mercaptoethanol and some carbonyl compounds in the presence of bentonite, using anhydrous benzene as the solvent, are summarized in the **table**, showing that the corresponding oxathiolanes are obtained in adequate yields.

In general, pure compounds were isolated, the work-up procedure is simple, and in addition the cost of the bentonite is low (9).

These experiments lead us to conclude that the catalyzed reaction with the bentonitic clay is an interesting new alternative for the production of oxathiolanes.

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9. Tonsil Actisil FF , Mexican clay , is available from Tonsil Mexicana SA de CV Insurgentes Sur 1971, CP 01020 Ciudad de México at US $ 00.95/kg *vs* [$ZnCl_2$ US $ 92.95/kg, $AlCl_3$ US $ 25.70/kg, $TiCl_3$ US $1082.00/kg, $BF_3{\cdot}Et_2O$ US $ 53.35/1Lt, $FeCl_3$ US $ 149.45/1g; taken from Aldrich 1995-1997, Catalogue].
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Received on November 8, 1997