

## Synthesis of 1, 3-oxathiolanes without use of organic solvent at room temperature. Remarkable functional selectivity

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### ABSTRACT/RESUME

**Abstract :** The aluminosilicates acids are efficient catalysts for the synthesis of oxathiolanes without solvent at room temperature. A functional selectivity was observed between aldehydes and ketones, aldehydes were transformed quantitatively. A functional selectivity has not been described before, it was observed within different aldehydes or within different ketones. This selectivity is important for the control of the reactions (activation or protection) of carbonyl compounds in organic synthesis.

### I. Introduction

The thioacetals and oxathioacetals are the most common groups, used to protect the aldehydes and ketones in organic synthesis multi-step. The dithioacetals and oxathio heterocyclic are a masked carbonyl compound vis-a-vis the nucleophilic attacks and plays an appreciable role in the new strategy for the electrophilic substitution of a hydrogen-carbon aldehyde group.

Different types of reagents have been used for the promotion of thioacetalization and oxathioacetalization of carbonyl compounds with Thiols and 2-Mercaptoethanol which of them APSG-HCl [1], H<sub>3</sub>PO<sub>4</sub>, HClO<sub>4</sub> [2], (BF<sub>3</sub>-OEt<sub>2</sub>) [3], ZrCl<sub>4</sub> [4], (SiO<sub>2</sub>-SOCl<sub>2</sub>) [5], (Amberlyst A15) [6], MoO<sub>2</sub>(acac)<sub>2</sub> [7], (TBAB) [8], (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>-SiO<sub>2</sub>) [9]. Schirini has recently used the silica sulfuric acid (SSA) [10], in refluxing hexane for the conversion of carbonyl compounds to 1,3-oxathiolanes.

### II. Experimental

Melting points (m.p) were determined with a Kofler hot apparatus and are uncorrected. Proton NMR spectra (PMR) were determined on Bruker AC 250 (250 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si). The IR spectra were recorded as KBr pellets on Perkin Elmer 16 PC FT-IR spectrometer UV-visible spectra ( $\lambda_{\max}$  log( $\epsilon$ )) were obtained with spectrophotometer Perkin-Elmer Lambda 15. Microwave irradiation were carried out with a commercial microwave oven (Toshiba ER 7620) at 2450 MHz. and with resonance cavity TE<sub>013</sub>, joined to a generator MES 73-800 of microwaves. Mass spectra were carried out on a Nermag Riber R10; TLC Analyses were performed by using Kieselgel Schleicher and Shull F 1500 Ls 254 and Merck 60F 254. The grinding of products were carried out on a analytical grinder A 10 of Janke and Kenkel-IKA Labortechnik. The Montmorillonite KSF was obtained from the firm of Súd Chemie. Zeolites (ZSM-5, LZYS62, 13X, DAY) as ammonium form were calcinated at 500°C under dry flow before use. (firm BDH, Linde, Linde Lancaster, Degusa).

## II.1. Preparation of zeolites exchanged $\text{h}^+$

**Procedure:** 10 g of Zeolite (ZSM5 or LZY562) are placed in a 50 ml flask and then treated with a solution of  $\text{NH}_4\text{Cl}$  (0.1 M) previously prepared with deionized water. The stoppered flask is allowed to stand overnight at room temperature. The solid residue was recovered by filtration and then activated in a muffle furnace at  $500^\circ\text{C}$  for 24 hours. The Zeolite in  $\text{H}^+$  ( $\text{H}^+$ -ZSM5,  $\text{H}^+$ -DAY or  $\text{H}^+$ -ZY562) is stored in a dry container

## II.2. Competition reactions

**Procedure:** Equimolecular quantities of the solid carbonyl compounds were dissolved in the minimum volume of methylene chloride mixed with one equivalent 2-mercaptoethanol and adsorbed on to  $\text{H}^+$ -Zeolite. The solvent was removed by evaporation in vacuo. All products were characterized by their IR and  $^1\text{H}$  NMR spectra. Yields of products were determined by  $^1\text{H}$  NMR spectroscopy.

**2-Nonyl-1,3-oxathiolane (1a')**: Prepared from Decanal (5 mmol; 0.68 g), Dodecanone (5 mmol; 0.92 g) and 2-mercaptoethanol (5 mmol, 0.41 g) in presence of  $\text{H}^+$ -LZY562 (3 g); colourless Liquid, Yield: (selectivity) 100 % ,  $\text{C}_{12}\text{H}_{24}\text{OS}$ ; calcd; C, 66.61 %, H, 11.18 %, S, 14.82 %, Found; C, 66.49 %, H, 11.12 %, S, 14.70 %; IR (neat)  $\text{cm}^{-1}$ : 1467, 1379, 1266, 1075, 1019 , 1030; NMR  $^1\text{H}$  ( $\text{CDCl}_3$ ): $\delta$ : 0.91 (s, 3H,  $\text{CH}_3$ ); 1.09-1.21 (m, 16H,  $\text{CH}_2$ ); 4.41 (m, 4H,  $\text{OCH}_2\text{CH}_2\text{S}$ ); 5.98 (s, 1H,  $\text{SCHO}$ ).

**2-Cyclohexyl-1, 3-oxathiolane (2a')**: Prepared from Carboxaldehyde (5 mmol: 0.56g), Cyclohexanone (5 mmol; 0,49g) and 2-mercaptoethanol (5 mmol; 0.41g) in presence of  $\text{H}^+$ -LZY562 (3g); Yield: (selectivity) 100 %,  $\text{C}_9\text{H}_{16}\text{OS}$ ; IR (neat)  $\text{cm}^{-1}$ : 1469, 1382, 1266, 1077, 1019), 1030; NMR  $^1\text{H}$  ( $\text{CDCl}_3$ )  $\delta$ : 1.06-2.07 (m, 11h, H Cyclohexyl) ; 4.35 (m, 4H,  $\text{OCH}_2\text{CH}_2\text{S}$ ); 4.85 (d, 1H,  $\text{SCH}$ ).

### 2-Phenyl-1, 3-oxathiolane (3a')

a) Prepared from Benzaldehyde (5 mmol: 0.53 g), Cyclohexanone (5 mmol; 0.49 g) and 2-mercaptoethanol (5 mmol, 0.41 g) in presence of  $\text{H}^+$ -LZY562 (3g); Yield: (selectivity) 100 %,  $\text{C}_9\text{H}_{10}\text{OS}$ .

b) Prepared from Benzaldehyde (5 mmol: 0.53 g), Decanal (5 mmol; 0.68g) and 2-mercaptoethanol (5 mmol, 0.41 g) in presence of  $\text{H}^+$ -LZY562 (3g); Yield: (selectivity) 100 %.

c) Prepared from Benzaldehyde (5 mmol: 0.53 g), Carboxaldehyde (5 mmol; 0.56 g) and 2-mercaptoethanol (5 mmol, 0.41 g) in presence of  $\text{H}^+$ -LZY562 (3g); Yield: (selectivity) 100 %;

d) Prepared from Benzaldehyde (5 mmol: 0.53 g), P-methoxy-benzaldehyde (5mmol; 0.68g) and 2-mercaptoethanol (5 mmol, 0.41g) in presence of  $\text{H}^+$ -LZY562 (3g); Yield: 47%.

e) Prepared from Benzaldehyde (5 mmol: 0.53 g), P-nitrobenzaldehyde (5 mmol; 1.10g) and 2-mercaptoethanol (5 mmol, 0.41 g) in presence of  $\text{H}^+$ -LZY562 (3g); Yield: 65%.

f) Prepared from Benzaldehyde (5 mmol: 0,53 g), Mesitaldehyde (5 mmol; 0,74g) and 2-mercaptoethanol (5 mmol, 0,41g) in presence of  $\text{H}^+$ -LZY562 (3g); Yield: 48%; IR: 2869, 1492, 1454, 1265, 1230, 1195, 1062, 1018, 972; NMR  $^1\text{H}$  ( $\text{CDCl}_3$ )  $\delta$ : 4.49-4.54 (m, 4H,  $\text{OCH}_2\text{CH}_2\text{S}$ ); 6.16 (s, 1H); 7.29-7.49 (m, 5H, H arom).

### 2-(4'-Methoxyphenyl)-1,3-oxathiolane (4a')

a) Prepared from P-methoxybenzaldehyde (5 mmol: 0.68 g), Acetophenone (5 mmol; 0.60g) and 2-mercaptoethanol (5 mmol, 0.41 g) in presence of  $\text{H}^+$ -Bentonite (3 g); Yellow Liquid, Te  $135^\circ\text{C}/1$  mm. Yield: (selectivity) 100%,  $\text{C}_{10}\text{H}_{12}\text{O}_2\text{S}$ .

b) Prepared from P-methoxybenzaldehyde (5 mmol: 0.68 g), Benzaldehyde (5 mmol; 0.53g) and 2-mercaptoethanol (5 mmol, 0.41 g) in presence of  $\text{H}^+$ -Bentonite (3 g); Yield: 53%; calcd; C, 61, 21 %, H, 6, 17 %, S, 16.35 %, Found; C, 60.91%, H, 6.23%, S, 16.12 % IR (neat)  $\text{cm}^{-1}$ : 1612, 1514, , 1262, 1176, 1029, 831;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 3.89 (s, 3H,  $\text{OCH}_3$ ); 4.69 (m, 4H,  $\text{OCH}_2\text{CH}_2\text{S}$ ); 5.92 (s, 1H,  $\text{SCHO}$ ); 6.87 (d, 2H, H arom); 7.18 (d, 2H, H arom).

### 2-(4'-Chlorophenyl)-1,3-oxathiolane (5a')

Prepared from P-chlorobenzaldehyde (5 mmol: 0.71 g), Diphenylacetone (5 mmol; 0.91 g) and 2-mercaptoethanol (5 mmol, 0.41g) in presence of  $\text{H}^+$ -LZY562 (3 g); Yellow Liquid, Te 122-125; Yield: (selectivity) 100 % ,  $\text{C}_9\text{H}_9\text{ClOS}$ ; calcd; C, 53.85 %, H, 4.51 %, S, 15.96 %, Found; C, 53.64%, H, 4.58 %, S, 15.78 %; IR (neat)  $\text{cm}^{-1}$ : 1598, 1496, 1414, 1209, 1091, 1015;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 4.67-4.70 (m, 4H,  $\text{OCH}_2\text{CH}_2\text{S}$ ); 5.93 (s, 1H,  $\text{SCHO}$ ); 7.02 (d, 2H, H arom); 7.21 (d, 2H, H arom).

### 2-(4'-nitrophenyl)-1,3-oxathiolane (6a')

a) Prepared from P-nitrobenzaldehyde (5 mmol; 1.10g), Anthrone (5 mmol; 0.97g) and 2-mercaptoethanol (5 mmol, 0.41g) in presence of  $\text{H}^+$ -ZSM5 (3 g); Colourless Solid, mp  $77-79^\circ\text{C}$ ; Yield: (selectivity) 100 % ,  $\text{C}_9\text{H}_9\text{NO}_3\text{S}$ ; b) Prepared from P-nitrobenzaldehyde (5 mmol; 1,10g), Benzaldehyde (5 mmol; 0.53g) and 2-mercaptoethanol (5 mmol, 0.41g) in presence of  $\text{H}^+$ -ZSM5 (3 g); Yield: 35%; calcd; C, 51.17 %, H, 4.28 %, N, 6.62 %, S, 15.16 %, Found; C, 51.29 %, H, 4.22 %, N 6.52 % S, 15.00 %; IR (Kbr)  $\text{cm}^{-1}$ : 1603, 1526, 1347, 1070, 866, 717;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 4.68-4.69 (m, 4H,  $\text{OCH}_2\text{CH}_2\text{S}$ ); 6.08 (s,

1H, SCHO); 7.58 (d, 2H, H arom); 7.79 (d, 2H, H arom).

**2-Thiophenyl-1,3-oxathiolane (7a')**: Prepared from Thiophene-2-carboxaldehyde (5 mmol; 0.56 g), Fluorenone (5 mmol; 0,90 g) and 2-mercaptoethanol (5 mmol, 0.41 g) in presence of H<sup>+</sup>-13X (3 g); Marron visqueux Liquid. Yield: (selectivity) 100 %, C<sub>7</sub>H<sub>8</sub>OS<sub>2</sub>; NMR <sup>1</sup>H (CDCl<sub>3</sub>) δ: 4.41 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>S); 5.40 (s, 1H, SCHO); 6.32-7.78 (m, 3H, H arom).

**2-(3,4-methylenedioxyphenyl)-1,3-oxathiolane(8a')**: Prepared from Piperonal (5 mmol: 0.75 g), Xanthene-9-one (5 mmol; 0.98 g) and 2-mercaptoethanol (5 mmol, 0.41 g) in presence of H<sup>+</sup>-DAY (3 g); Beige solid, mp, 62 °C. Yield: (selectivity) 100 %, C<sub>10</sub>H<sub>10</sub>O<sub>3</sub>S; NMR <sup>1</sup>H (CDCl<sub>3</sub>).δ:4.50 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>S); 5.03 (s, 1H, SCHO); 5.95 (s, 2H, OCH<sub>2</sub>O); 6.70-7.01 (m, 3H, H arom).

**2-(3',4'-Dimethoxyphenyl)-1,3-oxathiolane(9a')**: Prepared from Veratral (5 mmol: 0,83g), Thioxanthene-9-one (5 mmol; 1,06 g) and 2-mercaptoethanol (5 mmol, 0, 41 g) in presence of H<sup>+</sup>-ZSM5 (3 g); Beige Liquid, Te 153-155 °C/1 mm. Yield: (selectivity) 100 % , C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>S; IR (neat) cm<sup>-1</sup> : 1599, 1511, 1463, 1383, 1264, 1229, 1140, 1048, 1021, 858; <sup>1</sup>H NMR (CDCl<sub>3</sub>).δ: 3.87 (s, 3H, OCH<sub>3</sub>); 3.90 (s, 3H, OCH<sub>3</sub>); 4.71 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>S).

**2-(2,4,6-Trimethylphenyl)-1, 3-oxathiolane (10a')**:

a) Prepared from Mesitaldehyde (5 mmol; 0.74 g), Cyclododecanone (5 mmol; 0.91 g) and 2-mercaptoethanol (5 mmol, 0.41 g) in presence of H<sup>+</sup>-DAY (3 g); Yellow Liquid. Yield: (selectivity) 100 %, C<sub>12</sub>H<sub>16</sub>OS.

b) Prepared from Mesitaldehyde (5 mmol; 0.74 g), Benzaldehyde (5 mmol; 0.53 g) and 2-mercaptoethanol (5 mmol, 0.41 g) in presence of H<sup>+</sup>-DAY (3 g); Yield: 52%; NMR <sup>1</sup>H (CDCl<sub>3</sub>).δ: 2.19 (s, 3H, CH<sub>3</sub>); 2.23 (s, 3H, CH<sub>3</sub>); 2.32 (s, 3H, CH<sub>3</sub>) 4.59 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>S); 5.88 (s, 1H, SCHO); 6.79-7.51 (m, 2H, H arom);

**2-(4'-acetylphenyl)-1, 3-oxathiolane (11a')**: Prepared from P-acetylbenzaldehyde (5 mmol: 0, 71 g) and 2-mercaptoethanol (5 mmol, 0,41 g) in presence of H<sup>+</sup>-13X (3 g); Yield: (selectivity) 100% aldehyde, 0% cetone. C<sub>11</sub>H<sub>12</sub>OS; IR (KBR) cm<sup>-1</sup>: 3070, 2935, 2860, 1700(γ C=O), 1538, 1460, 1280, 1100, 940, 840; .NMR <sup>1</sup>H (CDCl<sub>3</sub>).δ: 2.5 (s, 3H, CH<sub>3</sub>); 4.41 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>S); 5.88 (s, 1H, SCHO); 7.29 (m, 4H, H arom).

**2-(2-Methyl, 2-phenyl)-1, 3- oxathiolane (1k')**:

a) Prepared from Acetophenone (5 mmol: 0.60 g), Cyclohexanone (5 mmol; 0.49 g) and 2-mercaptoethanol (5 mmol, 0.41 g) in presence of H<sup>+</sup>-KSF (3 g); Yellow Clear Liquid, Te 87°C/1, 2 mm Yield: (selectivity)100 % , C<sub>10</sub>H<sub>12</sub>OS;

b) Prepared from Acetophenone (5 mmol: 0.60 g), Diphenylcetone (5 mmol; 0.91 g) and 2-mercaptoethanol (5 mmol, 0.41g) in presence of H<sup>+</sup>-KSF (3 g); Yield: 40%; IR (neat) 1496, 1383, 1219, 1142, 1066, 769; .NMR <sup>1</sup>H (CDCl<sub>3</sub>). δ: 1.95 (s, 3H, CH<sub>3</sub>); 4.40 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>S); 7.29-7.48 (m, 13H, H arom).. 7.50-7.53 (m, 12H, H arom);

**2, 2-Diphenyl-1, 3-oxathiolane (2k')**:

a) Prepared from benzophenone (5 mmol: 0.91 g), cyclohexanone (5 mmol; 0, 49 g) and 2-mercaptoethanol (5 mmol, 0.41 g) in presence of H<sup>+</sup>-LZY562 (3 g); Yellow Liquid, Te 135°C/1 mm Yield: (selectivity) 100 % , C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>S;

b) Prepared from Benzophenone (5 mmol: 0.91g), Fluorenone (5 mmol; 0.90 g) and 2-mercaptoethanol (5 mmol; 0.41 g) in presence of H<sup>+</sup>-LZY562 (3 g); Yield: 40%;

c) Prepared from benzophenone (5 mmol: 0.91 g), Acetophenone (5 mmol; 0.60g) and 2-mercaptoethanol (5 mmol, 0.41 g) in presence of H<sup>+</sup>-LZY562 (3 g); Yield: 60%; IR (KBR) cm<sup>-1</sup> :1585 (γ C=C), 1030, 735 (δ CH, H arom monosub), 690 (γ C-S); .NMR <sup>1</sup>H (CDCl<sub>3</sub>).δ: 5.38 (s, 1H, (SC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>); 7.29 (m, 15H, H arom);

**2-fluorenyl-1, 3-oxathiolane (3k')**:

a) Prepared from fluorenone (5 mmol: 0.92 g), cyclopentanone (5 mmol; 0.40 g) and 2-mercaptoethanol (5 mmol, 0.41 g); Yellow solide, Yield: (selectivity) 100 %, C<sub>15</sub>H<sub>12</sub>OS.

b) Prepared from fluorenone (5 mmol: 0.92 g), benzophenone (5 mmol: 0, 91 g) and 2-mercaptoethanol (5 mmol, 0.41 g); Yield: 60%; IR (KBR) cm<sup>-1</sup> :1582 (γ C=C), 1030, 735, 692 (γ C-S); .NMR <sup>1</sup>H (CDCl<sub>3</sub>).δ: 4. 43 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>S); 7.29-7.98 (m, 8H, H arom).

### III. Results and descusion

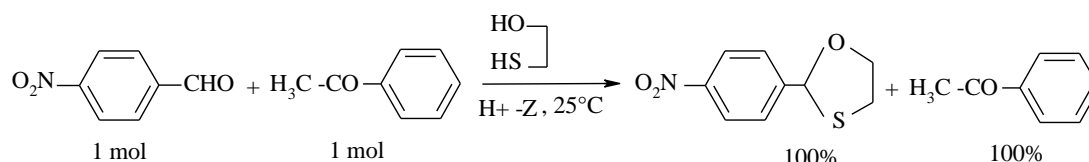
#### III.1. Competition reactions between aldehydes and ketones

Contrary to their oxygen analogous, the oxathioacetals are relatively stable in basic medium and can be easily hydrolyzed in acidic medium. We first have examined the intermolecular chemoselectivity by using an equimolar mixture of aldehyde and ketone and an equivalent of 2-mercaptoethanol by simple adsorption on zeolites at room temperature, according to the Fig.1.

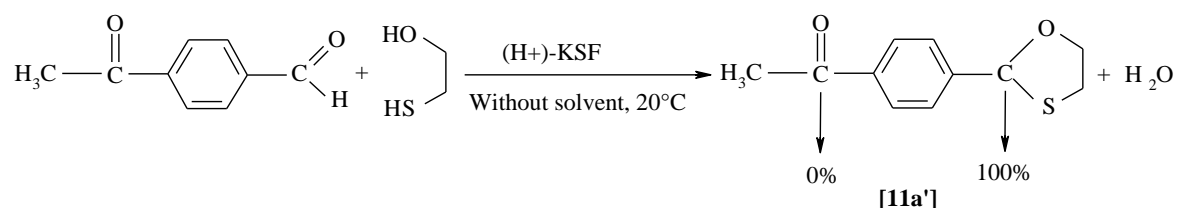
We have observed that only the aliphatic and aromatic aldehydes are converted into 1, 3-oxathiolanes corresponding with a quantitative conversion. The competitive reactions between aldehydes and ketones are regrouped in Table 1.

The equimolecular condensation of 4-Acetyl Benzaldehyde with 2-mercaptoethanol in the presence of H<sup>+</sup>-clay is leading to an intramolecular chemoselectivity. There is a formation of the

oxathiolane of the aldehyde function, while the ketone function remains unchanged, according to the Scheme.2.




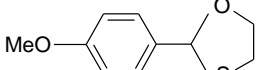
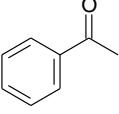
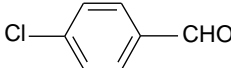
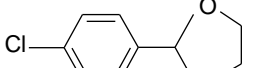
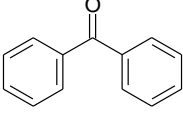
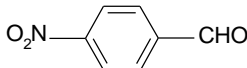
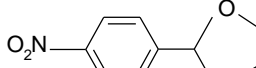
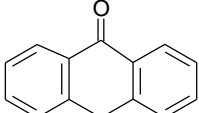
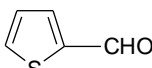
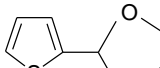
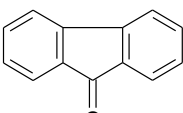

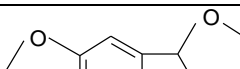
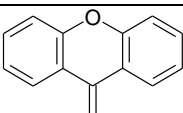
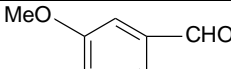
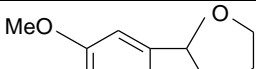
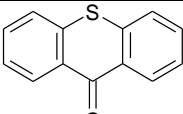
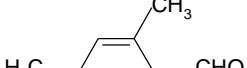
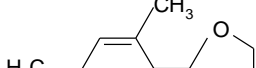
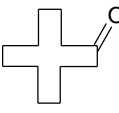
**Scheme 1.** Intermolecular chemoselectivity



**Scheme 2.** Intramolecular chemoselectivity

**Table 1.** Selectivity in competition reactions between Aldehydes [A] and Ketones [K] in formation of derivatives 1, 3-oxathiolanes. [A'] and [K']

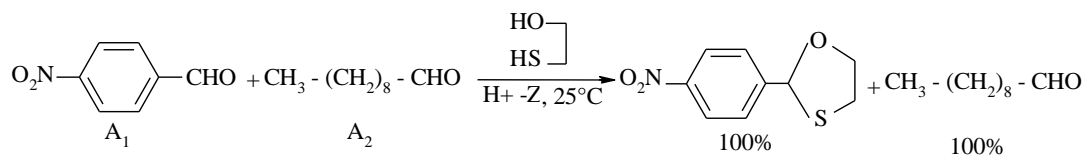
Aldehydes [A]	Ketones [K]	A' [100%]	K' [0%]
$\text{CH}_3 - (\text{CH}_2)_8 - \text{CHO}$ [1a]	2-Dodecanone	$\text{CH}_3 - (\text{CH}_2)_8 - \text{C} \begin{matrix} \diagup \text{O} \\ \diagdown \text{S} \end{matrix}$ [1a']	$\text{CH}_3 - (\text{CH}_2)_9 - \text{C}(\text{O}) - \text{CH}_3$
 [2a]	Cyclohexanone	 [2a']	 
 [3a]	Cyclohexanone	 [3a']	

 [4a]	Acetophenone	 [4a']	
 [5a]	Diphenylketone	 [5a']	
 [6a]	Anthrone	 [6a']	
 [7a]	Fluorenone	 [7a']	
 [8a]	Xanthone-9-one	 [8a']	
 [9a]	Thioxanthone-9-one	 [9a']	
 [10a]	Cyclododecanone	 [10a']	

## II.2. Competition reactions between aldehydes

The competition reactions between an equimolecular quantities of aliphatic aldehyde and an aromatic aldehyde with an equivalent of 2-mercaptoethanol in the presence of aluminosilicates

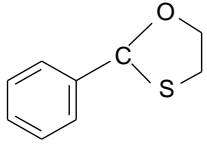
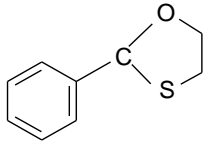
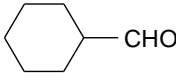
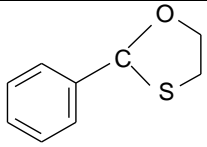
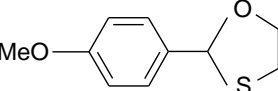
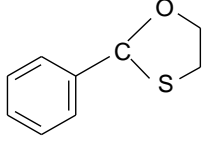
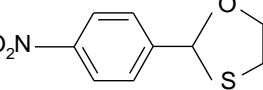
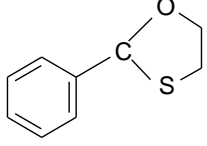
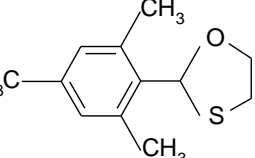
acids, show a noticeable and unexpected chemoselectivity. Only the derivative-1, 3-oxathiolane of the aromatic aldehyde is formed (Scheme.3).



**Scheme 3:** Scheme 3. Competition reactions between Aldehydes

The results of the selectivity between aldehydes are reported in Table 2.

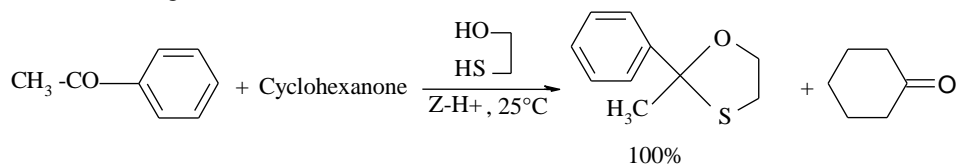
**Table 2.** Selectivity in competition reactions between Aldehydes (A<sub>1</sub> and A<sub>2</sub>) in formation of oxathiolanes.

Aldehyde 1 + Aldehyde 2		Selectivity	
[3a]	+ Decanal	 + $\text{CH}_3 - (\text{CH}_2)_8 - \text{CHO}$	 [3a'] 100% <span style="margin-left: 150px;">100%</span>
[3a]	+ Carboxaldehyde	 + 	 [3a'] 100% <span style="margin-left: 150px;">100%</span>
[3a]	+ p-Methoxy-benzaldehyde	 + 	 [3a'] 47% <span style="margin-left: 150px;">[4a'] 53%</span>
[3a]	+ p-Nitro-benzaldehyde	 + 	 [3a'] 65% <span style="margin-left: 150px;">[6a'] 35%</span>
[3a]	+ Mesitaldehyde	 + 	 [3a'] 52% <span style="margin-left: 150px;">[10a'] 48%</span>

We note a low electronic effect of groups carried by the aromatic. The electron-donor groups methoxy ( $\text{CH}_3\text{O}$ -) and methyl ( $-\text{CH}_3$ ) increase slightly the speed of reaction, thereby favoring the formation of derivatives-1, 3-oxathiolanes correspondents. The competition reaction between benzaldehyde and paranitrobenzaldehyde shows that the electron-acceptor group is slightly favoring the formation of (3a'). The determinant effect is in the presence or absence of the aromatic ring.

### III.3. Competition reactions between ketones

With regard to the ketones, their transformations are more slowly than aldehydes at room temperature and demands at least 24 hours. The conversion of aromatic ketones to derivative 1, 3-oxathiolanes is much faster than aliphatic ketones (Fig.4).

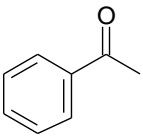
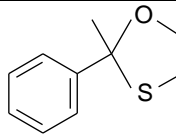
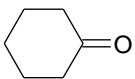
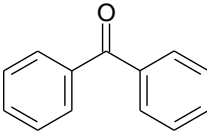
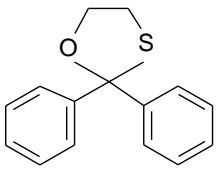
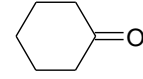
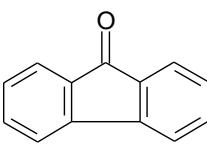
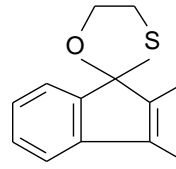
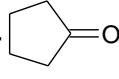
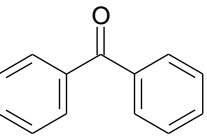
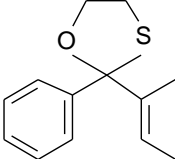
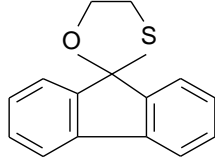
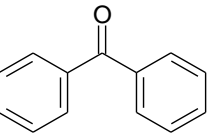
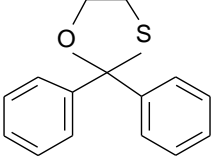
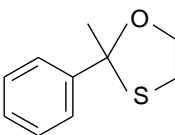
**Scheme 4.** Competition reactions between Ketones.

The competitions between different reactions of ketones (aliphatic and aromatic) are reported in Table 3.

Some formation reactions of 1, 3-dioxathiolanes are balanced. In order to determine if they are dealing with thermodynamic control that will determine the nature of the product, we have contacted in the

presence of zeolite H<sup>+</sup>-LZY562, 2-hexyl-1,3-oxathiolane and benzaldehyde for 8 hours to monitor the reaction in terms of thermodynamic or kinetic. We have not observed the formation of 2-phenyl-1, 3-oxathiolane, proving that the reaction is under kinetic control.

**Table 3.** Selectivity in competition reactions between Ketones (1 and 2) in formation of derivatives 1,3-oxathiolanes.

<b>Ketone 1</b>	<b>Ketone 2</b>	<b>Selectivity</b>
	+ Cyclohexanone	 +  [1K'] 100%      100%
	+ Cyclohexanone	 +  [2K'] 100%      100%
	+ Cyclopentanone	 +  [3K'] 100%      100%
	+ Fluorenone	 +  [2K'] 40%      60% [3K']
	+ Acetophenone	 +  [2K'] 60%      40% [1K']

## VI. Conclusion

Compared to conventional methods (homogeneous catalysis), all reactions were conducted at room temperature under favorable

conditions. The procedures have been simplified and improved (absence of pollution from different solvents and strong acids). A functional selectivity previously undescribed was observed between

different aldehydes or different ketones in the formation of derivatives 1, 3-oxathiolanes. The determinative effect is the presence or absence of aromatic rings. This may be related to the ease of aromatic molecules to slot between the aluminosilicate sheets. The lamellar nature of the montmorillonite clay as the phenomena of adsorption and desorption are for sure responsible for this selectivity.

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