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Environmentally desirable synthesis: one-pot and solvent free formation of arylidenes compounds from gem-diacetates

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ABSTRACT/RESUME

Abstract:*Heterogeneous acid catalysts are of importance in the fine chemicals area, and several been investigated in reactions such as the Knoevenagel reaction, an important reaction with pronounced solvent dependency. The condensation of active methylene compounds with gem-diacetates in the presence of acid aluminosilicates (montmorillonite KSF, K10/ZnCl$_2$) without solvent and under microwave irradiation, an efficient of synthesis of arylidenes compounds without isolation of aldehydes compounds. Cleavage of arylidene rhodanine derivative in position 5 in basic medium on Potassium Fluoride–Barium Oxide (BaO-KF) under focused microwave irradiation and free solvent is a simple and effective method for synthesis of, β-aryl-α-thiolacrylic acids.*

I. Introduction

Alkylidene and arylidene are found in many natural products and have an interesting antibiotics properties, the most famous is albonoursin**[1,2]**, isolated from fungal cultures. Besides their therapeutic properties (antiviral **[3, 4]**, antifungal **[3]**, antitumor**[3]**, sedative**[5]**, anesthetic**[5]**, hypnotic **[3]**, analgesic**[5]**), its arylidene's derivatives **[6,7]** are an important intermediates synthetic of the heterocyclic compounds**[8]** and the most convenient source of β-aryl α-thioacryliques acids [9].We reported herein that the condensation of active methylene compounds with benzylidenes-1,1- diacetates (acylals) catalysed by clay Montmorillonite without solvent takes place rapidly under focused microwave irradiation. The use of heterogeneous acid catalysts allows a simplification of the purification step to a simple filtration separating the catalyst from the reaction media.

II. Experimental

Melting points (m.p) were determined with a Kofler hot apparatus and are uncorrected. Proton NMR spectra (PMR) were determined on Brucker AC 250 (250 MHz, CDCl3, Me4Si).Th.; 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 and K10 was obtained from the firm of Sûd Chemie. Degusa). The IR spectra were recorded as KBr pellets on JASCO FT/IR-4100 spectrometer UV-visible spectra (λmax log(ε)) were obtained with Spectrophotometer of UV-Force of T60U. Microwave irradiation were carried out with a commercial microwave oven (Whirlpool WMC10007AW) at 2450 MHz. and with resonance cavity TEo13, joined to a generator MES 73-800 of microwaves. MES 73-800 of microwaves.

a) Preparation of Montmorillonite K10 Exchanged by Mn+

Procedure: In a 250 ml flask, the Montmorillonite K10 (20 g) was added to a solution of metallic salt $ZnCl_2$ (0.2 mol) dissolved in 100 ml of distilled water. The reaction al mixture was stirred for 24 h at room temperature. The suspension was washed twice with distilled water then centrifuged. The Montmorillonite exchanged by Zn^{2+}. Was washed with methanol and re-centrifuged. The solid was dried for 24 h in vacuum then finely ground. The final product was a clear beige color.

b) Preparation of the 1, 1 diacetoxy-1-(3, 4-methylenedioxyphenyl)methane (1)

Procedure: to a solution aromatic aldehyde (piperonal) (5 mmol) and freshly distilled acetic anhydride (5 mmol), montmorillonite KSF (3 g) was added at room temperature. The reaction mixture was magnetically stirred for 10 min. The resulting mixture was filtered. The filter cake was washed with CH_2Cl_2 (10 ml). The organic phase was dried over $MgSO_4$, filtered and the solvent was evaporated to give the pure desired compound as a white crystalline compound.

White solid crystallised in ethanol ; m. p = 79°C (lit[11]: 78 °C); $C_{12}H_{12}O_6$; MM = 252. 22 g. mol-1; Yield : 95 %; IR (KBr) cm-1 : 3080 (γ C-H), 1772 (γ C=O), 1602 (γ C=C); 1257 (γ CH_3OC=O); 1H NMR (CDCl3) δ: 2. 07 (s, 6H, CH_3); 6. 96 (s, 2H, OCH_2O); 7. 45 (d, 2H,) ; 8. 03 (s, 1H, CH=) ; MS, m/z (%): 252 (M+. 100).

Knoevenagel Condensation with gem diacetates in presence of solid acid

General procedure: The 1, 1 diacetoxy-1-(3, 4-methylenedioxyphenyl) methane (5 mmol) and the activated methylene compound (5 mmol) are mixed in the presence of montmorillonite KSF (5g) hydrated with a grinder for 2 minutes. The reaction mixture was placed in a 50 ml Erlenmeyer flask and then activated by irradiation with microwaves. After cooling of spent residue, dichloromethane (30 ml) is added to the vial to extract the solid acid by simple filtration through Celite. The solvent is evaporated under vacuum using a rotary evaporator. The product obtained was washed with ether to remove excess gem diacetate. After purification by distillation (Kugelhor), the solid obtained was identified by appropriate spectroscopic methods.

1-Condensation of 1,1-diacetoxy-1-(3,4-methylenedioxyphenyl)methane [1] with methylene acid compound using microwave heating (KSF);

2-(Benzo-1,3-dioxol-5-yl)methylene)-2H-inden-1, 3-dione: (1a)

Prepared from diacetoxy-1-(3, 4-methylenedioxyphenyl)methane (5 mmol: 1. 26 g) and 1, 3- indandione (5 mmol: 0. 73 g) in presence of KSF (5 g); Microwaves (P= 420 W, t = 08 min); Yellow Solid crystallised in ethanol ; m. p = 203 °C ; $C_{17}H_{10}O_4$; MM = 278. 26 g. mol^{-1}; Yield : 56 %; IR (KBr) cm^{-1} : 2982 (γ C-H), 1682 (γ C=O), 1590 (γ C=C); ^1H NMR ($CDCl_3$) δ; 6. 19 (s, 2H, OCH_2O); 6. 95 (d, 1H, H_2ar); 7. 11 (m, 1H $H_{2'}$ar); 7. 62 (m, 1H $H_{6'}$ar); 7. 85 (m, 4H, $H_{2, 3, 4, 5}$ ar); 7. 99 (m, 2H, $H_{2'}$aro); 8. 52 (s, 1H, CH); MS, m/z (%): 278 (M^+. 100); 279 (19. 07); 280 (2. 8).

5-(Benzo-1,3-dioxol-5-yl)methylene)-2, 2-dimethyl-1, 3-dioxane-4,6-dione: (1b)

Prepared from diacetoxy-1-(3, 4-methylenedioxyphenyl)methane (5 mmol: 1. 26 g) and Meldrum Acid , (5 mmol: 0. 72 g) in presence of KSF; Microwaves (P= 420 W, t = 12 min); Yellow Solid crystallised in ethanol ; m. p = 175 °C ; $C_{14}H_{10}O_6$; MM = 274. 22 g/mol; Yield : 59 %; IR (KBr) cm^{-1} : 2916 (γ C-H), 1748 (γ C=O),), 1717 (γ C=O), 1588 (γ C=C); ^1H NMR ($CDCl_3$) δ; 1. 62 (m, 6H, 2 CH_3); 6. 19 (s, 2H, OCH_2O); 7. 12 (m, 1H, H_2 ar); 7. 36 (m, 2H H_1ar); 7. 69 (s, 1H, CH); MS, m/z (%): 276 (M^+. 100); 277 (15. 7); 278 (2. 7).

2-(Benzo-1,3-dioxol-5-yl)methylene)-3,4-dihydronaphtalen-1(2H)-one: (1c)

Prepared from diacetoxy-1-(3, 4-methylenedioxyphenyl)methane (5 mmol: 1. 26 g) and α-Tetralone , (5 mmol: 0. 73 g) in presence of KSF (5 g); Microwaves (P= 520 W, t = 02 min); Yellow Solid crystallised in ethanol ; m. p = 75 °C ; $C_{18}H_{14}O_3$; MM = 278. 30 g/mol; Yield : 51 %; IR (KBr) cm^{-1} : 3060 (γ C-H), 2897 (γ CH_2), 1680 (γ C=O), 1600 (γ C=C), 1230 (γ C-O-C); ^1H NMR ($CDCl_3$) δ; 2. 19 (m, 4H, CH_2); 6. 1 (s, 2H, OCH_2O); 6. 9 (m, 1H, $H_{2'}$ ar); 7. 30 (m, 2H, $H_{1'}$ ar); 7. 4 (m, 2H, H_2 ar); 7. 47 (m, 1H, H_3 ar); 7. 7 (s, 1H, CH); 8 (m, 1H, H_1 ar); ^{13}C NMR ($CDCl_3$) δ; 26. 8 (CH_2), 39. 3 (CH_2), 101.7 (OCH_2O), 106. 8 ($C_{2'}$), 110. 5 (C_4), 124. 8 (C_1), 133. 6 (C_4), 137 (C_5), 144 (C_6); 148. 6 ($C_{4'}$); 188 (C=O); MS, m/z (%): 278 ($M^{+\cdot}$ 100); 279 (19. 8); 280 (2. 8).

3-3,4(methylenedioxy)phenylmethylene) -2, 4-(3H, 5H)furanedione: (1d)

Prepared from 1, 1 diacetoxy-1-(3, 4-methylenedioxyphenyl)methane (5mmol, 1. 26 g) and Tetronic acid [2, 4-(3H, 5H)furanedione] (5 mmol, 0. 5 g) in presence of KSF (5 g); Microwaves (P= 420 W, t = 3 min); Red Solid crystallised in ethanol ; m. p = 203°C; $C_{12}H_8O_5$; MM = 232. 18 g. mol^{-1}; Yield : 61 %; UV-Visible λ max log (ε) (EtOH) nm: 402 (3. 99); 282 (3.

75); 252 (3. 70); IR (KBr) cm^{-1} : 3010 (γ C-H), 1751 (γ C=O), 1690 (γ C=O), 1602 (γ C=C); ^1H NMR ($CDCl_3$) δ: 4. 65 (s, 2H, CH_2); 6. 20 (s, 2H, OCH_2O); 7. 13 (d, 1H, H_5 ar) ; 7. 8 (t, 1H, H_6 ar); 8. 03 (s, 1H, CH=) 8. 52 (m, 1H, H_2); MS, m/z (%): 232 (M+. 100); 233 (18. 7); 234 (2. 4).

2-Condensation of Bis(diacetoxy) methyl thiophene [2] with active methylene compound (K10/ZnCl₂)

<u>5-(2-thienylmethylene)-2-thioxo-4-thia- zolidinone: (2a)</u>

Prepared from bis(diacetoxy) methyl thiophene (5 mmol: 1. 07 g) and Rhodanine [2-Thioxo-4-thiazolidinone] (5 mmol, 1.67 g) in presence of K10/$ZnCl_2$ (5 g); Microwaves (P = 490 W, t = 4 min); Orange Solid crystallised in ethanol; m. p = 172 °C; $C_8H_5NOS_3$; MM = 163. 2 g. mol^{-1}; Yield : 79 %; UV-Visible λ max log (ε) (EtOH) nm: 257 (3. 75), 291 (4. 16), 401 (4. 64); IR (KBr) cm^{-1} : 1698 (γ C=O), 1615 (γ C=C). NMR ^1H (250 MHz, $CDCl_3$).δ: 7. 15 (m, 1H, H arom); 7. 35 (d, 1H, H arom); 7. 66 (d, 1H, H arom); 7. 87 (s, 1H, CH=C); 11. 50 (s, 1H, NH).

<u>5-(2-thienylmethylene)-3-methyl-2-thio- xo-4-thiazolidinone (2c)</u>

Prepared from bis(diacetoxy)methylthio-phene (5 mmol: 1.07 g) and 3-methylrhodanine (5 mmol, 0. 73 g) in presence of K10/$ZnCl_2$ (5 g); Orange solid cristallised in ethanol; Microwave (P= 490W, t= 5mn); m.p = 171 (lit[12]:170); $C_9H_7NOS_3$; MM = 241. 35 ; Yield : 84 %; UV-Visible λ max log (ε) (EtOH) nm: 254 (3. 72), 288 (4. 10), 395 (4. 60); IR (KBr) cm^{-1} : 1700 (v C=O) ,1620 (v C=C) ; ^1H NMR (250 MHz,$CDCl_3$). δ: 3. 45 (s, 3H, CH_3-N), 7. 10 (m, lH, H arom), 7. 30 (d, lH, H arom), 7. 60 (d, lH, H arom) ,7. 80 (s, lH, CH=C).

<u>5-(2-thienylmethylene)-2,4,6-(1H,3H,5H) pyrimidinetrione: (2b)</u>

Prepared from bis(diacetoxy) methyl thiophene (15 mmol: 3. 21 g) and barbituric acid [2,4,6(1*H*,3*H*,5*H*)-Pyrimidinetrione] (15 mmol, 1.92 g) in presence of K10/$ZnCl_2$ (5 g); Microwave (P= 490 W, t = 4 min); Red Solid cristallised in ethanol ; m. p = 272; $C_9H_6N_2O_3S$; MM = 222. 22 g/mol; Yield : 81%; UV-Visible λ max log (ε) (EtOH) nm: 254 (3.84), 259 (3. 79); 379 (3.98); IR (KBr) cm^{-1} : 3525-3575 (γ NH), 1752 (γ C=O), 1693 (γNHCONH) 1649 (γ C=O), 1553 (γ C=C). ^1H NMR ($CDCl_3$).δ: 7. 53 (m, 1H, H ar); 8. 20 (m, 2H, H ar); 8. 55 (s, 1H, CH=); 11. 32 (s, 1H, NH).

Cleavage of 5-arylidene rhodanine with Potassium Fluoride–Barium Oxide (BaO-KF)

General procedure: potassium fluoride–barium oxide (BaO-KF) (3g) is added to a solution of 5-arylidene rhodanine *(5* mmol) in methylene chloride. After evaporation of the solvent under vacuum, the solid is irradiated with microwaves (490 W, 4-5 mn). Water (15 ml) was added and filtered. The filtrate was acidified to pH = 2 with hydrochloric acid and the β-thienyl-α-thiolacrylic acid acid was isolated by filtration. The acid is crystallized in ethanol.

β-thienyl-α-thiolacrylic acid:

Yellow solid cristallised in ethanol; Microwave (P= 280 W, t = 4 min); m.p =116°C; $C_7H_7O_2S$; MM = 155.19 g/mol; Yield : 93%; UV-Visible λ max log (ε) (EtOH) nm: 232 (3.65). 251 (3.53). 261 (3.52). 268 (3.52). 337 (4.09) ; IR (KBr) cm^{-1} : 2580, 2638 (ν SH),1672 (νC=O),1595 (νC=C);^1H NMR (250 MHz, $CDCl_3$) : 4.64 (s, lH, SH) , 7.00-7.59 (m, 3H, H arom) , 8.11 (s, lH, CH) ,8.72 (m. lH, CO_2H)

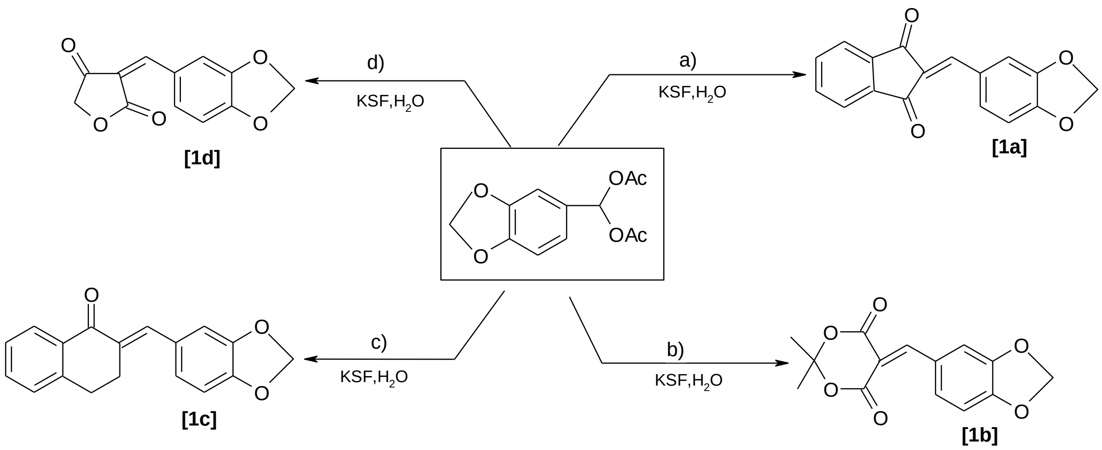
III. Results and descusion

In our work, we mainly used the KSF with high acidity of Brônsted. Starting from the idea that the hydrolysis of esters during esterification reactions catalyzed by KSF clay under microwave irradiation has already been done by the authors, we hypothesized that water molecules intercalated in the Montmorillonite KSF, highly polar and strongly activated by microwave, were responsible for the hydrolysis reaction in situ of diacetates.

We have prepared arylidenes compounds from 1,1-diacetate piperonyl methane **(1),** by reaction "one-pot" with compounds have an acidic methylene, under microwave irradiation.(Scheme-1) Gem diacetate is impregnated on Montmorillonite KSF by dissolution in methanol, followed by evaporation of the solvent in vacuo. A trace of water added to the solid mixture before irradiation.

The reaction is rapid and reproducible. After three minutes of irradiation at 420 W in a simple microwave trading, the yield is 61%. The procedure is greatly simplified compared to heating at reflux with the use of sulfuric acid.

The reaction produces two molecules of acetic acid. Montmorillonite KSF is a Bronsted acid catalyst in condensation reactions with aldehydes.
The results of the condensation are reported in Table 1.



Scheme 1. *Condensation of 1, 1-Diacetate piperonyl methane with active methylene acid catalyzed by KSF;*
a) 1, 3-Indandione; b) Meldrum acid; c) α-Tetralone; d) Tetronic Acid

Table 1. *Condensation of 1,1-diacetoxy-1-(3,4-methylenedioxyphenyl)methane with methylene acid compound using microwave heating (KSF);*

y_1 y_2	**Microwave**		**Product**	**Molecular formula**	**color**	**m.p (°C)**	**Yield (%)**
	P(W)	**t(mn)**					
1, 3 Indandione	420	8	**1a**	$C_{17}H_{10}O_4$	Yellow	203	56
Meldrum acid	420	12	**1b**	$C_{14}H_{12}O_6$	Yellow	176	59
α-Tetralone	520	2	**1c**	$C_{18}H_{14}O_3$	Yellow	75	51
Tetronic Acid	420	3	**1d**	$C_{12}H_8O_5$	Red	203	61

Faced with average yields ranging from 50% to 61 % with clay protonated (Mont-H^+), we thought of using a Lewis acid catalyst. Substituting the proton by the zinc cations in the K10, then obtained a Lewis acid catalyst (K10-$ZnCl_2$) non hydrolysable, unlike the $ZnCl_2$ alone is very sensitive to water. These can form the pillars between the layers it is adapted better to catalyze the formation of the corresponding arylidenes from bis (diacetoxy) methylthiophene **(2).**

The literature review of furfurylydenes derivatives and thienylydenes showed a less experienced. Their synthesis from the corresponding carbonyl compounds in acidic homogeneous medium is poorly reproducible. Our work was to find a replacement base for access to arylidenes compounds in the Knoevenagel reaction with active methylene compounds. The use of this new supported catalyst has allowed condensing in dry conditions under microwave activation a variety of active methylene compounds (Scheme.2)

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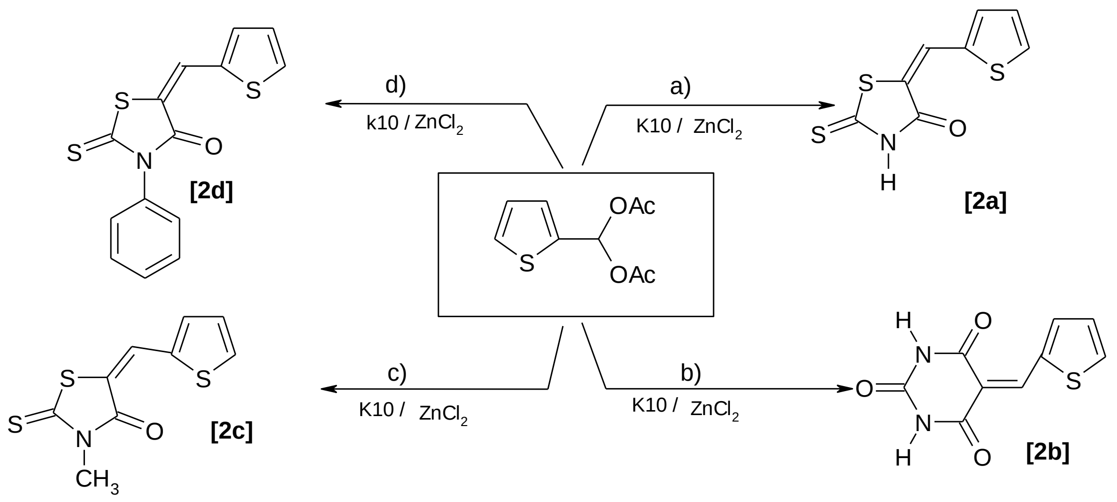


Scheme 2: *Condensation of bis(diacetoxy) methyl thiophenewith active methylene acid catalyzed by K10/ZnCl$_2$; a) Rhodanine; b) 3-Methyl rhodanine ; c) 3-Phenyl rhodanine*

The results obtained are shown in Table.2

Table 2 . *Condensation of Bis(diacetoxy)methyl thiophene with active methylene compound K10/ZnCl$_2$)*

y1 / y2	Microwave		Product	Molecular formula	color	m.p	Yield (%)
	P(W)	**t(mn)**					
Rhodanine	490	4	**2a**	$C_8H_5NOS_3$	Orange	172	79
Barbituric Acid	490	4	**2b**	$C_9H_6NO_3S$	Red	272	81
3-methylrhodanine	490	5	**2c**	$C_9H_7NOS_3$	Orange	171	84
3-phenylrhodanine	490	5	**2d**	$C_{14}H_9NOS_3$	Orange	175	75

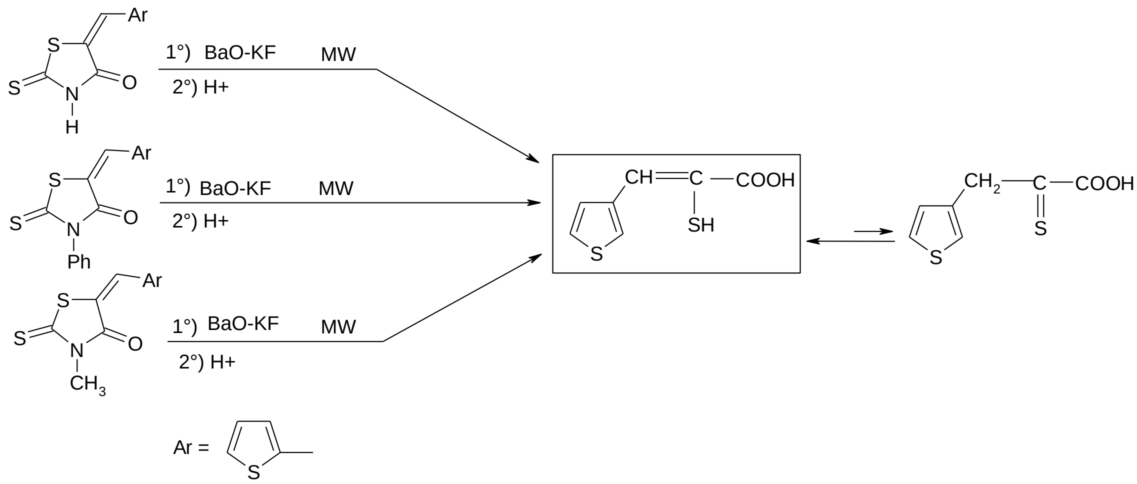
According to the results, we found that the doped solid acid catalysis better by zinc cations and under the same conditions training arylidenes with significant yield increases ranging from 75 % to 79 %.

Cleavage of 5-arylidene rhodanine compound with Potassium Fluoride–Barium Oxide (BaO-KF).

Cleavage of arylidene rhodanine derivative in position 5 in basic medium on potassium fluoride–barium oxide (BaO-KF) under microwave irradiation and free solvent is a simple and effective method for synthesis of, β-aryl-α-thiolacrylic acids.

We were inspired by the literature that the cleavage takes place with heated alkali hydroxide, barium hydroxide at 100°C [10]. After acidification derivative β-aryl-α-thiolacrylic acids were obtained.

We report herein the cleavage of 5-arylidene-2-thioxo-4-thiazolidinonbesy by potassium fluoride–barium oxide (BaO-KF). By activation under microwave irradiation (490 W, 4-5 min)(Scheme-3). Extraction with water and acidification gave β-thienyl-α-thiolacrylic acid with yield (93%). The β-thienyl-α-thiolacrylic acid can exist in two tautomeric forms: β-thienyl-α-thiolacrylic acids [form (A)] or as β-thienyl-α-thiopyruvic acids [form (B)]. Spectroscopic data and chemical properties are in favourlh of the predominance of form (A): In the 1H NMR spectrum no signal for the benzyl group appears and the resonance at 4. 64 ppm was attributed to the SH.



Scheme 3. Cleavage of 5-arylidene rhodanine derived with potassium fluoride–barium oxide (BaO-KF)

IV. Conclusion

A general method was designed for the one pot synthesis of arylidenes compounds from gem diacetates whit acidic methylene a study on Knoevenagel reaction under acid heterogeneous conditions without solvent and under microwave irradiation. This method, using montmorillonite KSF (Brônsted acid) and doped montmorillonite by Zinc (Lewis acid) is very efficient and much more rapid than classical methods. Compounds with potential synthetic and biological interest are synthesized.
These compounds can be cleaved with potassium fluoride–barium oxide (BaO-KF) into β-thienyl-α-thiolacrylic acids in quasiquantitative yields, which is a reaction intermediate for the synthesis of many reaction compounds (amino acid, nitriles acid, and amines)

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