A GREEN TRANSFORMATION OF KETONES INTO DIOXOLANES BY TUNISIAN ACID ACTIVATED CLAY UNDER SOLVENT FREE: EXPERIMENTAL AND THEORETICAL STUDIES

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RESUME: Nous avons étudié la condensation de l'éthylène glycol **1** avec une série de méthylcétones **2a-e**, en présence de l'argile activée à l'acide **HA** sans solvant et sous pression autogène. Les structures des 2-méthyl-2-(R)-dioxolanes **3a-e** ont été déterminées par spectroscopie de RMN ^{1}H et ^{13}C. Les géométries les plus stables de ces composés ont été alors déterminées et caractérisées par des calculs en utilisant le programme Gaussian 03. Les géométries de ces composés ont été entièrement optimisées au niveau DFT en utilisant la fonctionnelle B3LYP et la base 6-31G(d,p) et identifiées comme minimum sur la surface d'énergie potentiel au même niveau de la théorie. Un bon accord est alors obtenu entre les résultats expérimentaux et théoriques. D'autre part, nous avons proposé le mécanisme de la formation des dioxolanes **3** par acétalisation des méthylcétones **2** catalysées par les sites acides de Brönsted et de Lewis localisés à la surface active de l'argile activée à l'acide **HA**.

Mots clés : argile tunisienne activée à l'acide, dioxolane, charge atomique, charge de Mulliken, calcul de la FDT.

ABSTRACT: We have studied the condensation of ethylene glycol **1** and a series of methylketones **2a-e** in the presence of the acid activated clay **HA** without solvent and under autogeneous pressure. The structures of 2-methyl-2 -(R)-dioxolanes **3a-e** were characterized by ^{1}H and ^{13}C NMR spectroscopy. These compounds were fully optimized at DFT level of theory with the functional B3LYP and 6-31G (d,p) basis set as minimum on the potential surfaces at the same level of theory. The more stable geometries of these compounds have been determined and characterised. A good agreement was then obtained between the experimental and theoretical results. Moreover, we have proposed the mechanism of the formation of dioxolanes **3** by acetalization of methylketones **2** catalysed by Bronsted and Lewis acid sites localized on the active surface of the acid activated clay **HA**.

Key words: Tunisian acid activated clay, dioxolane, atomic charge, Mulliken charge, DFT calculation.

INTRODUCTION

Bronsted acids, commonly used in organic synthesis, have major disadvantages such as their corrosive natures and harmful. Moreover, the green chemistry limits the production of pollutants while reducing health risks. Replacement of liquid acids by solid acids has a high interest in these last years. Since, they are efficient catalysts, available, inexpensive, easily extracted of the reaction media, reusable and non-polluting compared to homogeneous systems. Several works described the use of

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different solid catalysts as alumina, silica gel, supported silica, zeolites, pillared clays and acid activated clays [1,2].

Most of these catalysts are inorganic supports [3,4], especially clay materials which have many advantageous properties [5]. These clay materials subjected to several chemical treatment such as mechanical activation methods [6], intercalating [7], thermochemical treatment [8,9] well as chemical activation [10,11] to get a very special adaptation to employment well-defined treated clays as adsorbents [12], bleaching agents for vegetable oils [13] and in the domain of pollution control [14,15].

On the other hand, Tunisian clays have been attracting increasing attention due to their significant roles as potential catalysts for the organic reaction [16-19]. Indeed, we have studied the acetalization of acetone into 2,2-dimethyl-1,3-dioxolane by ethylene glycol in the presence of pillared clays aluminum, zirconium and cerium under free solvent and autogenous pressure [20] and various acid activated clays [21]. We have showed also that the last acid clays catalyzed the conversion of pure ethylene glycol into 2-methyl-1,3-dioxolane [22] and its condensation with aromatic aldehydes to lead 2-R-1,3-dioxolanes [23].

Organic reactions were carried out at atmospheric pressure in solvent-free system, under microwave irradiation or ultra-sound to save energy and decrease the time reaction [24,25]. Besides, other works were also conducted under high, reduced and/or autogenously pressure to decrease temperature and avoid the decomposition of substrate side-reactions [26-28].

In this present study, we will focus on the behaviour of the ethylene glycol with a series of methylketones over Tunisian acid activated clay which available and inexpensive.

RESULTS AND DISCUSSION

The acid activated clay **HA** is prepared from the crude clay which is extracted from Djebel Haidoudi of the region of Gabes of the Tunisian South-East. The chemical composition of these clays was determined by non-destructive techniques for the analysis of solids. The structural changes in the activated clay were identified by X-ray diffraction DRX and infrared spectroscopy IR. In fact, the analysis of X-ray diffractogram of the crude clay **H** (Figure 1) indicates the presence of two rays at 3.35 Å and 4.26 Å concerning quartz. Their intensities increase with the duration of the acid activation (Figure 2). The presence of the ray at 12.62 Å shows that the clay **H** is a smectite, as well as, the characteristic rays of the Kaolinite at 7.18 Å and 4.26 Å.

Moreover, the IR spectrum represented in the Figure 3 showing two that the bands at 3689 cm^{-1} and 695 cm^{-1} and reveals the presence of crystalline kaolinite in crude clay **H** [29]. The presence of bands located at 3620 cm^{-1} and 902 cm^{-1} respectively are attributed to

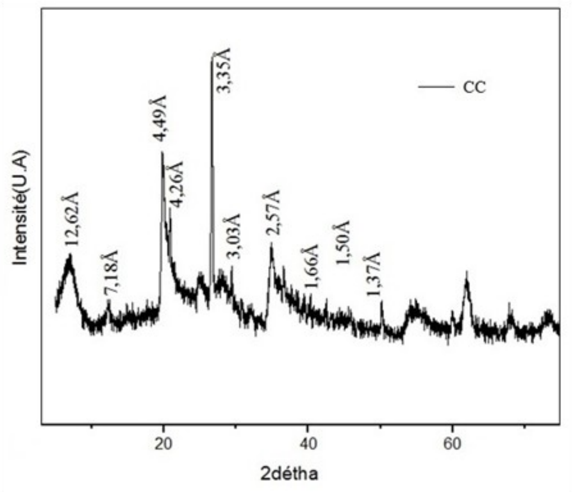


Figure 1. X-ray diffractogram of the crud clay **H**.

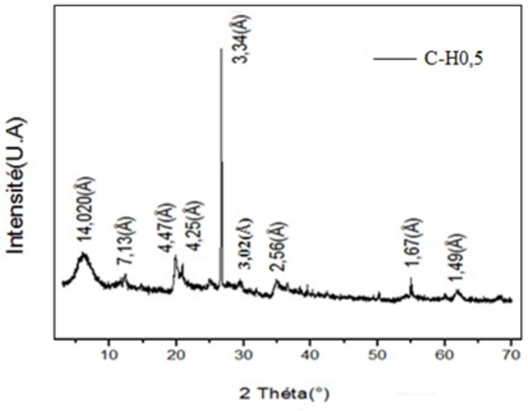


Figure 2. X-ray diffractogram of the acid activated clay **HA**.

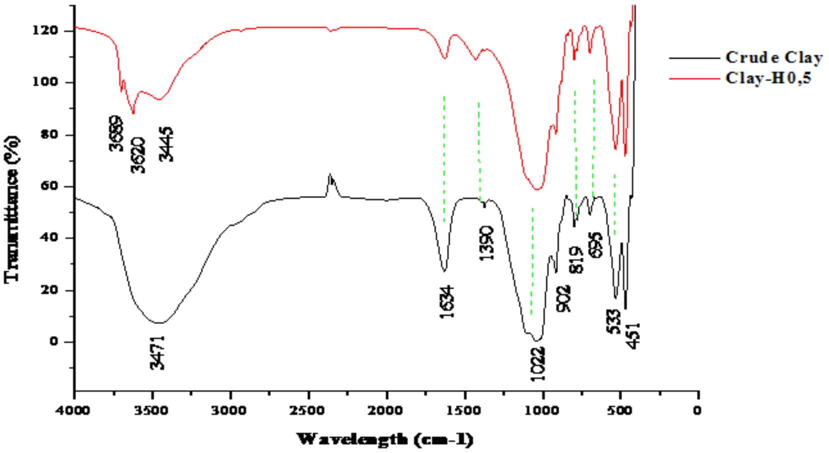


Figure 3. Infrared spectrum of the crud clay **H** and acid activated clay **HA**.

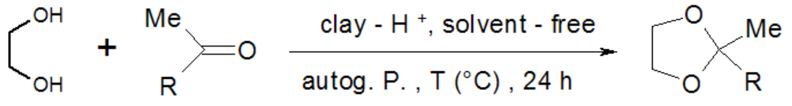
the stretching vibration and deformation of the Al-OH bands and indicates that this clay is a dioctahedral smectite [30]. The decrease in the intensity of the band to 3620 cm^{-1} characteristic of the Al-O-Al bonds indicates the gradual release of Al^{3+} ion [31]. The disappearance of this band after acid treating of raw clay **H** confirms the attack on the octahedral layer which is also showed in elemental analysis of the acid activated clay **HA** [32]. The band located at 1022 cm^{-1} is characteristic of stretching vibration of Si-O group of clay, while deformation of the strips appears respectively at 451 cm^{-1}, for the group Si-O [33], at 819 cm^{-1} for Fe-OH and 695 cm^{-1} for Mg-OH [34]. The low intensity of these last bands indicates that the magnesium and iron in clays **H** and **HA** are at low concentration. The bands located at 1634 cm^{-1} and 3445 cm^{-1} are assigned to the deformation and vibrations valence of the O-H band of water [33].

Elemental analysis of clay **H** and **HA** determined by atomic adsorption, show that it is relatively rich in silica and alumina (Table I). The study of the chemical composition of clays **H** and **HA** proves extraction of cations interfolliaires Al^{3+}, Fe^{3+}, Mg^{2+} to afford a substantial increase in the acidity of the surface of the clay and has given the highest

Table I. The physico-chemical and mineralogical characteristics of the clays **H** and **HA**.

Clay	**SiO_2** (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MgO (%)	**CEC** (meq/100g)	**S_{BET}** (m^2/g)	**PV** (cm^3/g)	**NSA** (mmol/g)
H	49,06	16,05	9,06	3,02	75	78,24	0.186	0,300
HA	58,12	14,11	6,29	2,14	35	186,1	0.281	0,786

CEC: cation exchange capacity ; **BET**: specific surface ; **NSA**: number of acid sites ; **PV**: Porous Volume.



1 **2** **3**

a: R= C_6H_5 ; **b:** R= CH_3 ; **c:** R= CH_3CH_2 ; **d:** R= $C_6H_5CH_2$; **e:** R=$ClCH_2$

Scheme 1. Reaction of ethylene glycol **1** with methylketones **2** into dioxolanes **3** in the presence of acid activated clay **HA**.

Table II. The more stable configurations and main characteristics of methylketones **2**.

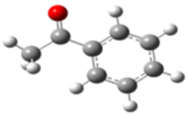
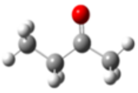
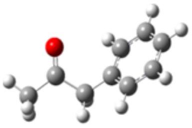
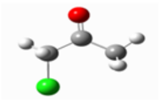
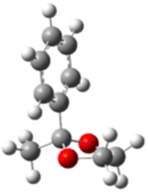
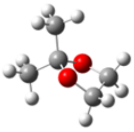
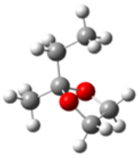
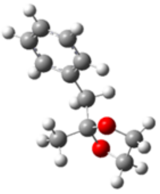
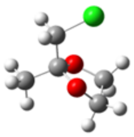
Configuration	 **2a**	 **2b**	 **2c**	 **2d**	 **2e**
$AC_{\underline{C}=O}$ (u.a)	0.393	0.421	0.427	0.431	0.437
$AC_{C=\underline{O}}$ (u.a)	-0.454	-0.428	-0.436	-0.426	-0.417
$\delta_{\underline{C}=O}$ (ppm)	197.75	206.57	208.60	206.05	199.64
$\delta_{C\underline{H}_3C=O}$ (ppm)	2.50	2.17	2.18	2.03	2.30
$\delta_{\underline{C}H_3C=O}$ (ppm)	26.42	30.70	28.77	29.09	26.51

Table III. The more stable configurations and main characteristics of 2-methyl-2-R-dioxolanes **3**.

Configuration	 **3a**	 **3b**	 **3c**	 **3d**	 **3e**
T (°C)	140	40	70	140	110
Yield (%)	8	12	21	30	55
AC_{C2} (u.a)	0.455	0.494	0.503	0.517	0.504
$\delta_{C\underline{H}_3C2}$ (ppm)	1.65	1.37	1.01	1.25	1.45
$\delta_{\underline{C}H_3C2}$ (ppm)	27.66	25.92	22.71	24.15	22.14
$\delta_{\underline{C}2}$ (ppm)	108.77	108.19	108.49	109.44	108.07

number of Bronsted acid sites NSA. The acid activation of the clay **H** leads to an increase in specific surface area BET and their acidity that obtains a maximum but decreased the cation exchange capacity CEC.

Thus, we have investigated the effect of acid activated clay **HA** on the mixture of ethylene glycol **1** and methylketones **2a-e** without solvent in an autoclave under autogenous pressure, at the desired temperature and during 24 h (Scheme 1).

Hence, the acetophenone **2a** and acetone **2b** are among less reactive substrates with the respect of the diol **1** and gave the dioxolanes **3a** and **3b** in low yields (8% and 12%). The replacement of methyl group by other electron -donating substituents as ethyl and benzyl groups improve the yields in **3c** (21%) and **3d** (30%). By contrast, the use of chloroacetone **2e**, which is more reactive than previous ketones due to the attractor inductive effect of chlorine atom, favors then the acetalization reaction proceeds and it leads to the corresponding dioxolane **3e** in satisfactory yield (55%). Based on the present methodology, the synthesis of 2-methyl-2-R-dioxolanes **3a-e** depends closely on several parameters such as electronic effects and steric hindrance of aliphatic and aromatic substituents of the methylketones **2a-e** (Tables II and III). On the other hand, it must be noticed that Pério et al. [35] have also obtained 2-phenyl-2-methyl-1,3-dioxolane **3a** with low yield (13%) by acetalization of acetophenone **2a** with ethylene glycol **1** in the presence of PTSA under solvent-free and under microwave irradiation [36].

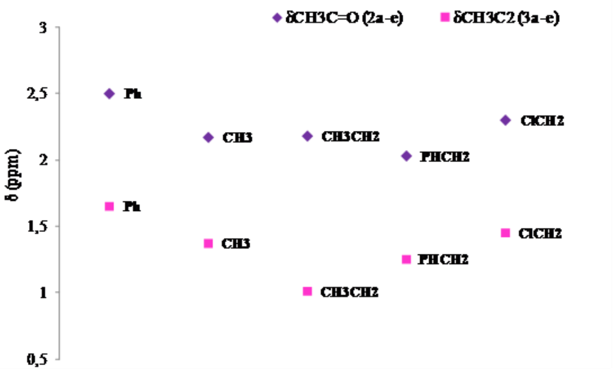


Figure 4. Chemical Shifts of protons of substrates **2** and their products **3**.

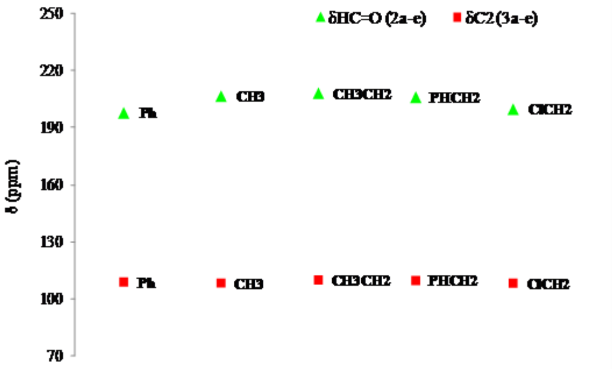


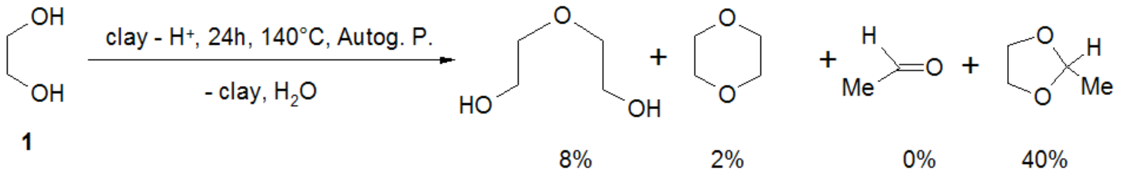
Figure 5. Chemical Shifts of carbons of substrates **2** and their products **3**.

All compounds **2a-e** and **3a-e** were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy (Tables II and III). The protons of $C\underline{H}_3C_2$ of dioxolanes **3a-e** appear in more upfield than those protons of precursor methyl group of methylketones **2a-e** (Figures 4 and 5). Moreover, the carbons of $CH_3\underline{C}_2$ of hetrocycles **3a-e** appear in more downfield than those precursor $\underline{C}=O$ of ketones **2a-e**.

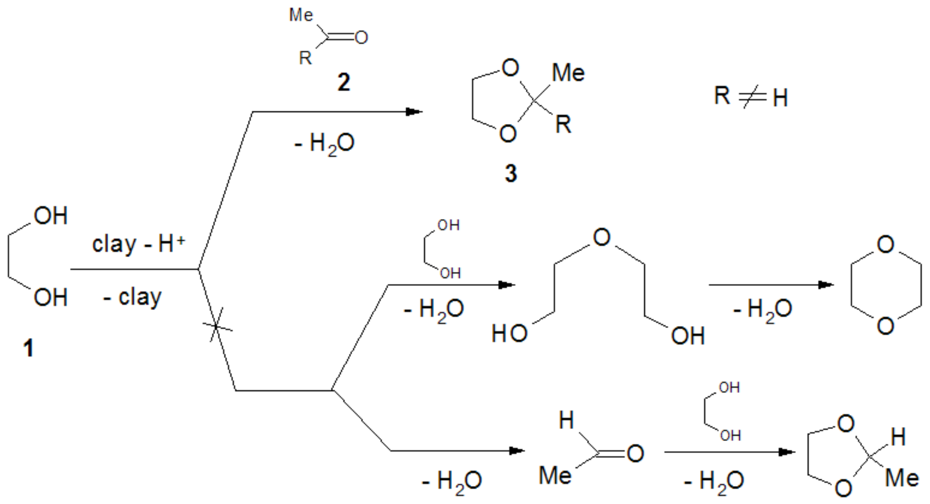
Recently, we have reported [23] that the heating of pure ethylene glycol **1** in the presence of clay **HA** under the same experimental condition gave a mixture of diethylene glycol, 1,4-dioxane and 2-methyl-1,3-dioxolane (Scheme 2).

However, we have not detected the last products in crudes of the reaction of ethylene glycol **1** with methylketones **2a-e** over acid activated clay **HA**. To explanation of this unexpected result, we can consider that the fast solvation of the hydroxyl groups of glycol **1** by the carbonyl group of the reagent **2** prevents its adsorption on the surface solid catalyst and consequently its acid rearrangement into the corresponding products **3** (Scheme 3).

Previously, we have calculated the atomic charges of oxygen carbon atoms of the carbonyl group in aldehydes and of the C2 carbon of dioxolanes using the method DFT/ B3LYP with the 6-31G(d,p) basis set and using Gaussian 03 program [37]. These interesting results led us in this present work to calculate the atomic charges at the same atoms of methylketones **2a-e** and 2-methyl-2-R-dioxolanes **3a-e** by means of the same level of theory. The tables II and III represented the most stable geometries of thus dioxolanes **3a-e** which determined and characterised as



Scheme 2. Transformation of ethlylene glycol **1** over acid activated clay **HA**.



Scheme 3. Selective acetalization of ethylene glycol **1** by ketones **2** with clay **HA** into dioxolane **3**.

minimum on the potential surfaces. The results reported in Figures 6 and 7 demonstrated that the atomic charges on the carbon of C=O group of ketones **2a-e** are lower than those of quaternary carbon C2 of dioxolanes **3a-e**. Moreover, it must be noticed that these results are in perfect agreement with those cited by Gopinath et al. [38]. In fact, theses authors calculated the electron density at the carbonyl carbon of aldehydes and ketones using the semi-emperical molecular orbital AM1 method as implemented in the Hyperchem package (Hyperchem, Inc., Gainsville, FL). A good agreement is then obtained between the experimental results and the theoretical ones.

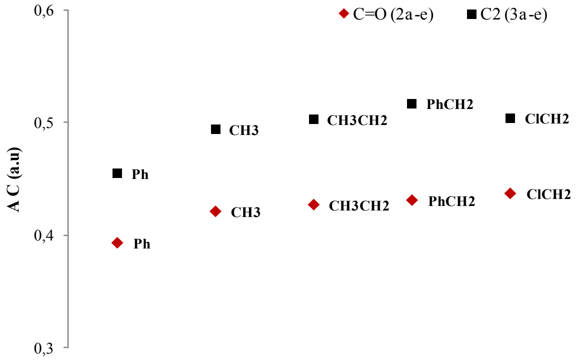


Figure 6: Atomic charges of <u>C</u>=O and C2 carbons of reagents **2** and their products **3**.

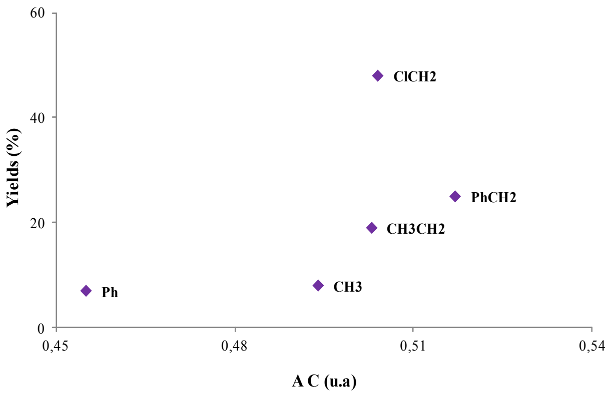
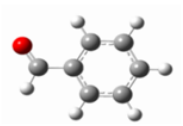
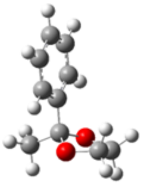
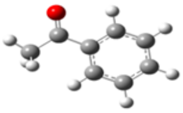
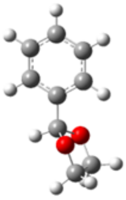


Figure 7: Curves of atomic charges of <u>C</u>=O and C2 carbons of reagents **2** and their products **3**.

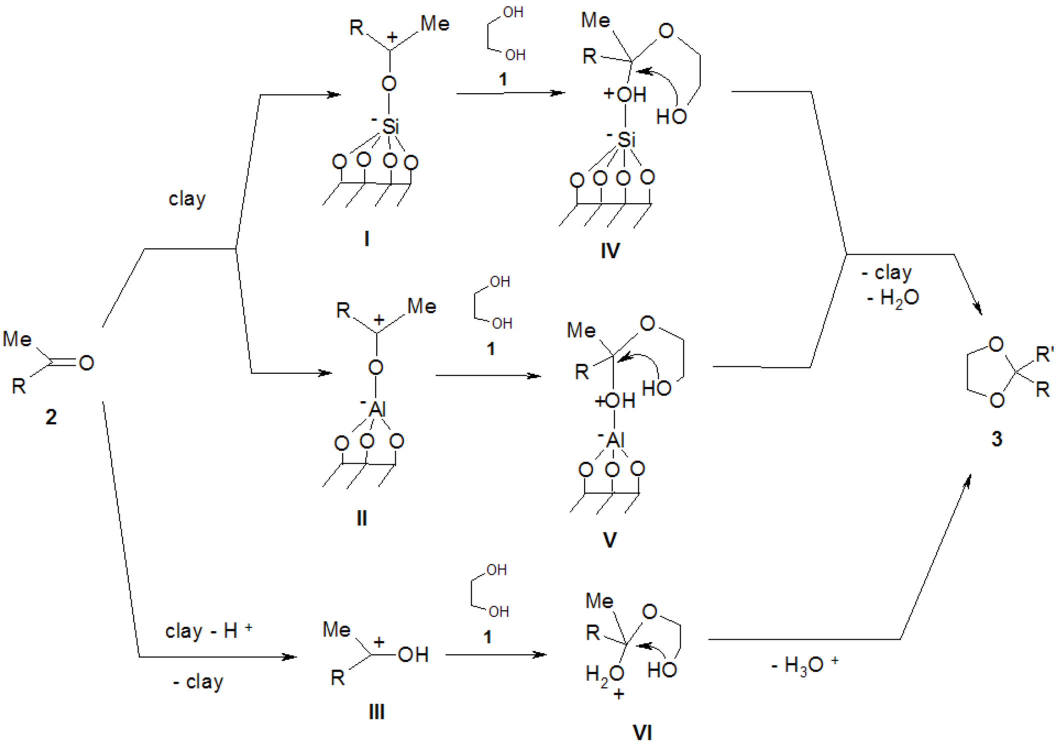
We have already mentioned in our previous work [19] that the acetalization of benzaldehyde under the same experimental conditions leads to 2-phenyl-1,3-dioxolane with 23% yield. However, we have obtained in this work 2-methyl-2-phenyl-1,3-dioxolane from acetophenone with 7% yield. This very large difference in reactivity between the two aromatic carbonyl compounds with respect to ethylene glycol **1** could be explained that the steric hindrance of the methyl group is more important than the donor inductif effect (Table 4). In fact, the study revealed that the stereochemical position of the aromatic cycle is different in these two dioxolanes.

On the other hand, we have reported that acid activated clays transformed *N*-acyl-2,2-dimethylaziridines into mixture of oxazolines, N-methallylamides and amidoalcohols *via* protonated aziridinium ion, pentacoordinated silicates and tetracoordinated aluminates

Table IV. More stable configurations and atomic charges of benzaldehyde and acetophenone and their derivatives dioxolanes.

Aromatic carbonyl compounds	$A\,C_{C=\underline{O}}$	$A\,C_{\underline{C}=O}$	Yield (%)	Aromatic dioxolanes	$A\,C_{C2}$
	-0.416	0.258	23		0.353
	-0.454	0.393	8		0.455

A C: Atomic Charge



Scheme 4. Mechanism proposed of acetalization of methylketones **2** with ethylene glycol **1** catalyzed by acid activated clay **HA**.

intermediates [17,18]. From the last mechanism we can then suggest another mechanism to explain the acetalization of methylktones **2** and ethylene glycol **1** over Tunisian acid activated clay **HA** (Scheme 4). The First step in this catalytic process represents the adsorption of the substrate **2** on the active surface clay **HA**. Secondly, the formation of the coordinate bond between the acceptor sites Lewis of the clay **HA** and the oxygen atom of the ketone **2** leads to the formation of pentacoordinated silicate **I** and tetracoordinated aluminate **II** intermediates. Thus, ethlylene glycol **1** attacks the last intermediates **I** and **II** to give the corresponding zwitterions **IV** and **V** which cyclized into dioxolanes **3** and regenerates the wet clay. Ketone **2** is also catalyzed by Bronsted acid sites located on the active surface of the protonated clay to form the carbonium ion **III**. The additition of ethlylene glycol **1** on this last intermediate **III** leads to dioxolanes **3** *via* the oxonium ion **VI**.

CONCLUSION

In this work, we have developed a new heterogeneous catalyst for the synthesis of dioxolanes from ketones in satisfactory yields and under optimal experimental conditions in respect of green chemistry. The NMR spectroscopic studies and the theoretical calculations are in good agreement with the experimental results of the acetalization reaction. It seems that the electronic and steric hindrance effects of substitutents of ketones **2a-e** plays also a significant role on the synthesis of 2-methyl-2-R-1,3-dioxolanes **3a-e**.

EXPERIMENTAL SECTION

The ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AC spectrometer (300 MHz ^{1}H frequency). The ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AC spectrometer (75 MHz ^{13}C frequency). Chemical shifts of the most atoms of compounds **2a-e** and **3a-e** are reported in ppm from internal TMS.

All theoretical calculations were performed using the Gaussian 03 program. Complete geometry optimizations were carried out on all compounds under study in the gas phase, and then a frequency calculation was carried out to check that the optimized structure is indeed a minimum. The methods of the density functional theory with the functional B3LYP were used. The polarized double zeta basis set 6-31G (d,p) was then used. The atomic charges were calculated from Mulliken population analysis (MPA).

Typical procedure of the preparation of the acid activated clay HA

1. Preparation of the crude clay: 100 g of crude clay are dispersed in 30 mL of distilled water and then subjected to a vigorous stirring until the complete homogenization of the suspension. After separation of all organic matrixes, raw clay is dried and crushed in an agate mortar to obtain particles of 100 µm or less.

2. Preparation of the acid activated clay HA: 15 g of raw clay are warmed in reflux in 150 mL of a solution of HCl (3 N) during 0.5 h. After cooling and filtration, this clay is washed by the distilled water under centrifugation (3500 r/mn). Water was changed to eliminate chlorides, carbonates and quartz. After filtration, the acid activated clay **HA** is dried at 60 °C during few days before crushing.

3. Synthesis of dioxolane 3: An autoclave (100 mL) was loaded with 55 mmol of ethylene glycol **1**, 50 mmol of carbonyl compound **2** and 50 mg of acid activated clay **HA**. The mixture is heated at desired temperature for 24 h under autogenous pressure. After cooling, wet acid clay **HA** is separated by filtration. The organic layer is washed with distilled water to remove ethylene glycol **1**. After drying ($MgSO_4$), the solvent is evaporated under vacuum. The dioxolane **3** is then obtained.

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