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EXPERIMENTAL AND THEORETICAL INVESTIGATION ON THE CATALYTIC ACETALIZATION OF ALDEHYDES OVER TUNISIAN ACID ACTIVATED CLAY: A MECHANISTIC STUDY

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RESUME: La synthèse d'une série de 2-(R)-dioxolannes **3a-f** a été réalisée par acétalisation des aldéhydes insaturés **2a-f** avec l'éthylène-glycol **1**, en présence d'une argile Tunisienne activée à l'acide HA en absence de solvant. Tous les composés ont été entièrement optimisés au niveau DFT de la théorie à la B3LYP fonctionnelle et 6-31G (d, p) un ensemble de base. Puis, les géométries les plus stables de **2a-f** et **3a-f** ont été déterminées. Les calculs théoriques des charges atomiques sur le groupe carbonyle C=O des aldéhydes **2a-f** et le carbone C-2 des dioxolanes **3a-f** objet d'une enquête ont été effectuées en utilisant l'analyse de population de Mulliken avec la méthode DFT. Tous les calculs ont été effectués avec le programme Gaussian 03. Un bon accord a été ensuite obtenu entre les résultats expérimentaux et théoriques. En effet, ces résultats suggèrent que les produits **3a-f** sont formés par la réaction des réactifs **1** et **2a-f** avec les sites acides de Bronsted et les sites accepteurs de Lewis localisés à la surface active de l'argile HA. Les intermédiaires concurrents, tels que la silice pentacoordonée **I**, l'alumine tétracoordonnée **II** et le carbocation **III**, conduisent aux dioxolanes **3a-f** et régénèrent l'argile humide correspondante.

ABSTRACT: The synthesis of a series of 2-(*R*)-dioxolanes **3a-f** was performed by acetalization of insatured aldehydes **2a-f** with ethylene glycol **1** in the presence of Tunisian acid activated clay HA under solvent-free conditions. All compounds were fully optimized at DFT level of theory with the functional B3LYP and 6-31G (d,p) basis set. Then, the most stable geometries of **2a-f** and **3a-f** were determined. The theoretical calculations of the atomic charges on the carbonyl group C=O of the aldehydes **2a-f** and C-2 carbon of the dioxolanes **3a-f** under investigation were carried out using the Mulliken population analysis with the DFT method. All calculations were performed with the Gaussian 03 program. A good agreement was then obtained between the experimental and theoretical results. Indeed, these results suggest that products **3a-f** are formed by the reaction of the reagents **1** and **2a-f** with Bronsted acid sites and Lewis acceptor sites localized on the active surface of clay HA. The competing intermediates such as pentacoordinated silica **I**, tetracoordinated alumina **II** and carbocation **III** lead to the dioxolanes **3a-f** and generated the corresponding wet clay.

Keywords: acetalization, acid activated clay, atomic charge, Mulliken charge, DFT calculation.

INTRODUCTION

Acid activated montmorillonite clay promotes organic reactions such as limonen conversion, cationic ring opening polymerization of glycosides, isomerization of α-pinene, dehydration of glucose, the synthesis of derivatives of 5β-pregnam-3α-ol, 1,2-proton migration of chalcone epoxyde and reaction of methyl diazoacetate with various aldehydes [1-8]. The protection of aldehydes and

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ketones into the corresponding dioxolanes was also achieved from orthoformates, 2,2-dimethyl-1,3-dioxolane or ethylene glycol in the presence of montmorillonites K10 and KSF [9-11].

On the other hand, Tunisian clays have been attracting the attention of our researchers because of their significant roles as potential catalysts in organic reactions [12]. Previously, we had used acid activated clays to transform ethylene glycol into 2-methyl-1,3-dioxolane through acetaldehyde [13]. Similarly, oxazolidines have been synthesized by condensation of 2-amino-2-methylpropanol with various carbonyl compounds in the presence of these clays [14].

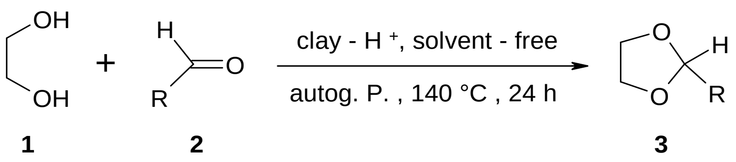
In this present study, we will focus on the behaviour of ethylene glycol (EG) **1** with insaturated aldehydes **2a-f** over Tunisian acid activated clay which is easily available and inexpensive.

RESULTS AND DISCUSSION

In the first stage, we used acid activated smectic clay from the raw clay which is native of Djebel Haidoudi of the Tunisian Southeast [13]. The acid activated Haidoudi clay is prepared by heating to reflux of mixture of the raw clay and chloride acid (3 M) for 0.5 h. This last modified material is then named clay HA.

Based on the present methodology, the synthesis of the dioxolanes **3a-f** depends closely on several parameters such as electronic effects and steric hindrance of substituents of the substrates **2a-f**, reaction conditions and the nature of clay HA used ($S_{BET} = 186\ m^2\ g^{-1}$).

Hence, we have treated a mixture of EG **1** and a series of cinnamaldehyde **2a** and various para-substituted benzaldehydes **2b-f** by catalytic amount of clay HA to prepare the corresponding monosubstituted dioxolanes **3a-f**. All the reactions were carried solvent-free in an autoclave under autogenously pressure during 24 h at 140 °C.



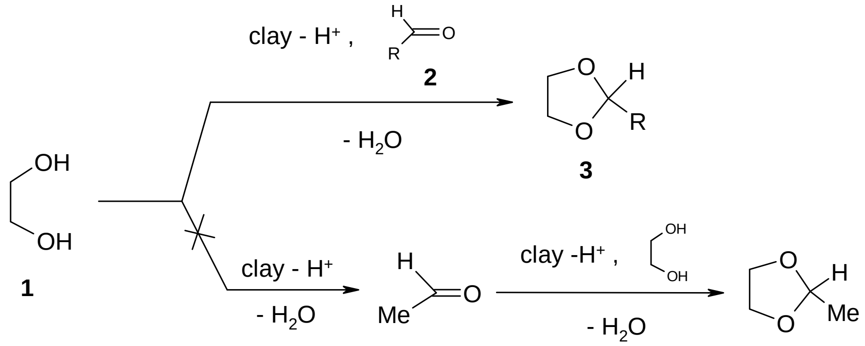
	R
2a , **3a**	Ph-CH=CH
2b , **3b**	*p*-$CH_3OC_6H_4$
2c , **3c**	*p*-$CH_3C_6H_4$
2d , **3d**	C_6H_5
2e , **3e**	*p*-ClC_6H_4
2f , **3f**	*p*-$NO_2C_6H_4$

Scheme 1. Formation of dioxolanes **3** from reagents **1** and **2** in the presence of clay HA.

We have observed that the conjugated and aromatic aldehydes **2a-e**, carrying the electron-donating groups by inductive and mesomeric effects, lead to dioxolanes **3a** and **3b** in modest yields (11% and 14%) and dioxolanes **3c** and **3d** in moderate yields (17 and 23%). The formation of the dioxolane **3e** (29%) from *p*-chlorobenzaldehyde **2e** shows that, in the case of chlorine atom, the donor mesomeric effect prevailed then the attractor inductive effect. More interestingly with *p*-nitrobenzaldehyde **2f**, the presence of an electron-withdrawing substituent makes the carbon of the carbonyl group more electrophilic by a mesomeric effect and the yield (72%) of dioxolane **3f** increases intensively.

Our results are in good agreement with those cited by Pério et al. [9]. They have reported that the treatment of EG **1** by *p*-nitrobenzaldehyde **2f** in the presence of PTSA under solvent-free and microwave irradiation leads to **3f** with the yields of 93% [15]. Other works have reported that catalysts, carrying various Si/Al ratios such as hydrophobic Al-MCM-41 and sulfonic acid-functionalized FSM-16 mesoporus, are used for synthesize dioxolanes [16].

Moreover, it must be noticed that no trace of 2-methyl-1,3-dioxolane was detected in the crude after the treatment of the mixture of EG **1** and aldehydes **2a-f** with clay HA. As for an explanation of this result, we can consider the fast solvation of the hydroxyl groups of EG **1** by the carbonyl group of **2a-f**. This solvation prevents the adsorption of EG **1** on the surface solid catalyst and consequently its acid dehydration into the acetaldehyde. 2-methyl-1,3-dioxolane could not then be formed by attack of a second molecule of EG **1** on this intermediary product expected. Therefore, we propose that EG **1** reacted only with aldehydes **2** present in the acid medium to give the corresponding dioxolanes **3**.



Scheme 2. Selective acetalization of ethylene glycol **1** by carbonyl compound **2** into dioxolane **3**.

All carbonyl compounds **2a-f** and dioxolanes **3a-f** were characterized by ^{1}H NMR and ^{13}C NMR (Tables I and II).

Besides, the protons $\underline{H}C_2$ of dioxolanes **3a-f** appear in more upfield than those corresponding protons of aldehydes **2a-f**.

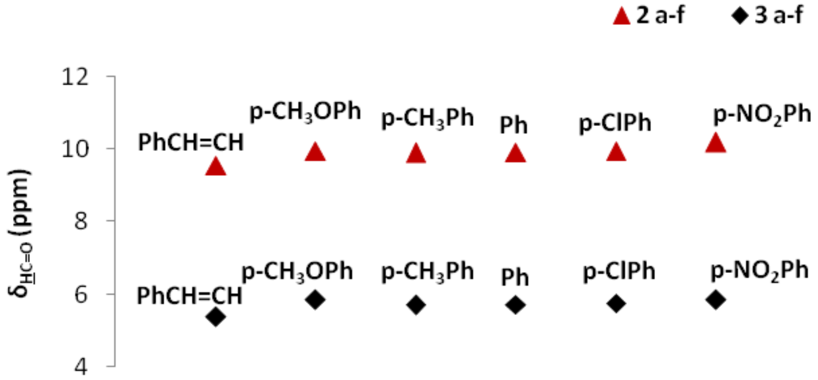
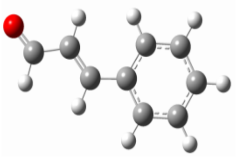
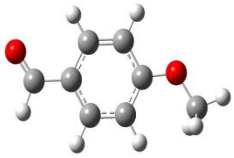
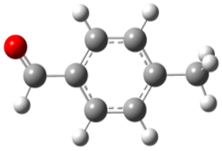
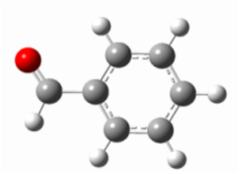
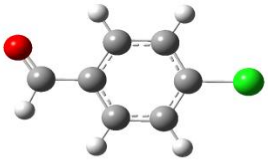
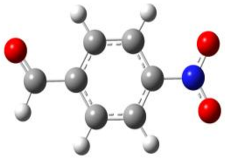


Fig. 1: Evolution of ^{1}H chemical shifts of aldehydes **2a-f** and dioxolanes **3a-f**.

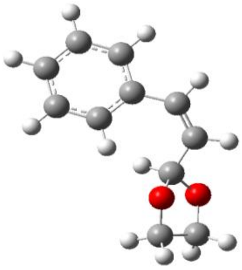
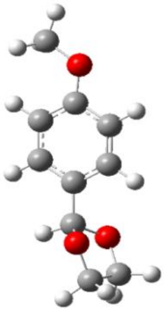
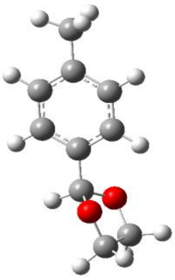
Table I. The most stable configurations and atomic charges of aldehydes **2**.

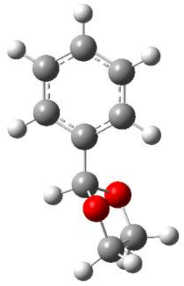
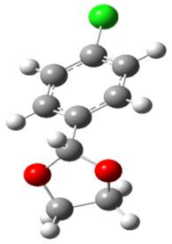
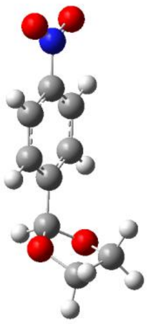
aldehyde	configuration	$\delta_{\underline{H}C=O}$ (ppm)	$\delta_{H\underline{C}=O}$ (ppm)	A C $_{C=\underline{O}}$	A C $_{\underline{C}=O}$
2a		9.55	194.05	-0.431	0.282
2b		9.95	190.71	-0.427	0.253

aldehyde	configuration	$\delta_{\underline{H}C=O}$ (ppm)	$\delta_{H\underline{C}=O}$ (ppm)	A $C_{C=\underline{O}}$	A $C_{\underline{C}=O}$
2c		9.90	192.02	-0.420	0.256
2d		9.92	192.94	-0.416	0.258
2e		9.96	190,94	-0.413	0.261
2f		10.18	190.37	-0.399	0.263

A C: Atomic Charge

Table II. The most stable configurations of 2-R-1,3-dioxolanes **3a-f**.

dioxolane	yield (%)	configuration	$\delta_{\underline{H}C2}$ (ppm)	$\delta_{H\underline{C}2}$ (ppm)	A C_{C2}
3a	14		5.37	103.70	0.389
3b	11		5.85	103.73	0.350
3c	17		5.70	103.64	0.352

dioxolane	yield (%)	configuration	δ_{HC2} (ppm)	δ_{HC2} (ppm)	A C_{C2}
3d	23		5.72	103.67	0.353
3e	29		5.76	102.94	0.362
3f	72		5.85	102.25	0.369

A C: atomic Charge

Moreover, the carbons of $\underline{C}$=O group of **2a-f** appear in more downfield than those corresponding carbons of $H\underline{C}_2$ of **3a-f**.

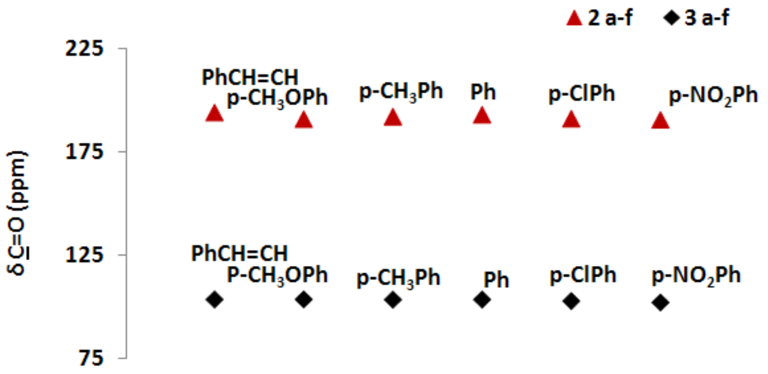


Fig. 2 : Evolution of ^{13}C chemical shifts of aldehydes **2a-f** and dioxolanes **3a-f**.

Previously, we have calculated the atomic charges at the carbon and oxygen of amide group of N-acylaziridines using the method DFT/B3LYP with the base 6-31G (d) of Gaussian 98 program [17]. In this work we calculated the atomic charges of the oxygen and carbon of the carbonyl group in aldehydes **2a-f** and of the C-2 carbon of dioxolanes **3a-f** under investigation, by means of the same level of theory (Tables I and II). The most stable geometries of **2a-f** and **3a-f** have been determined and characterized as minima on the potential surfaces [18].

The Gaussian 03 program has been used for all calculations presented in this work [19]. A good agreement is then obtained between the experimental results and the theoretical ones. The results summarized in Figure 3 demonstrated that the atomic charges on the carbon of C=O group of aldehydes **2a-f** are lower than those of C-2 tertiary carbon corresponding of dioxolanes **3a-f**. One important point to note is that, in the case of ethylene glycol **1,** higher negative charge was found on oxygen site (-0.551) which proves the strong nucleophility of this heteroatom.

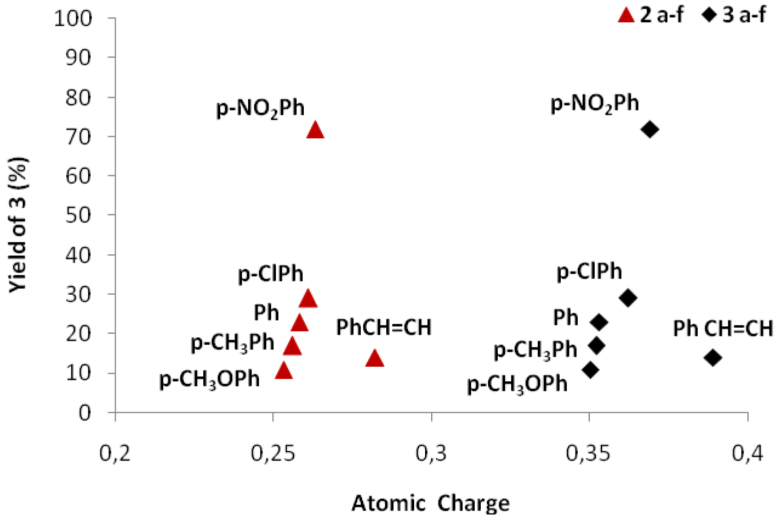
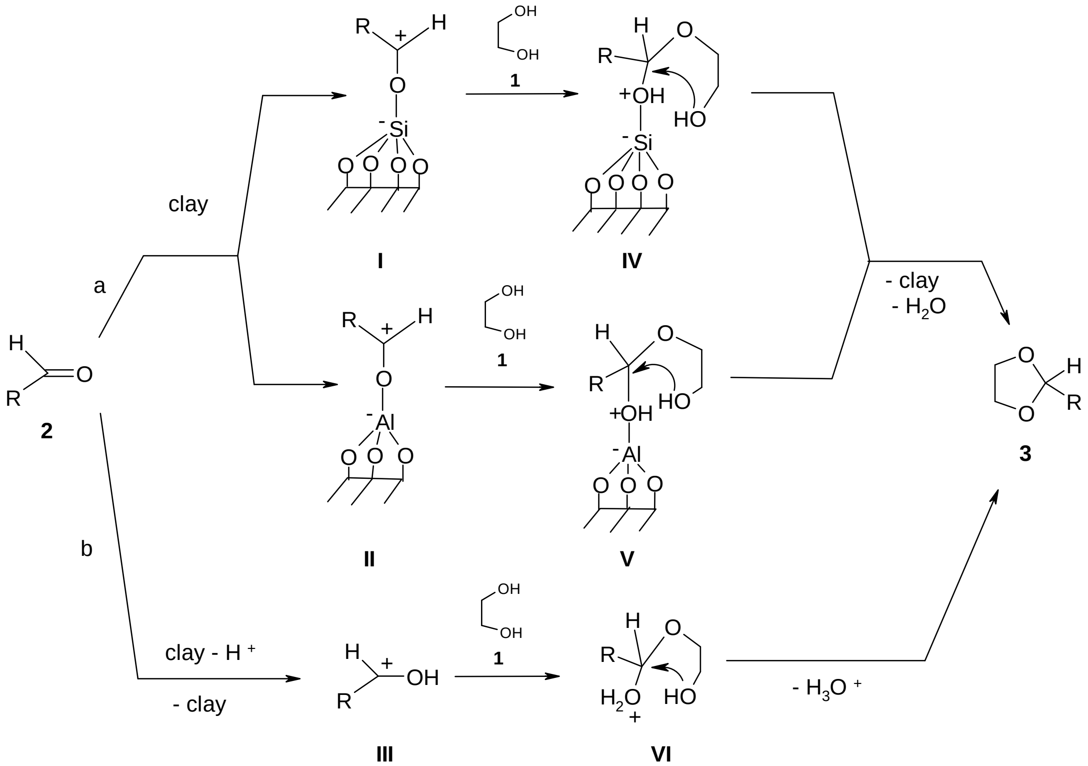


Fig. 3. Evolution of the yield of **3** according to the atomic charge of C=O of **2a-f** and C2 of **3a-f**.

Besides, it must be noticed that these results are in perfect agreement with those cited in the literature. Indeed, Gopinath et al. [20] calculated the electron density at the carbonyl carbon of aldehydes using semi-emperical molecular orbital calculations, the AM1 method as implemented in the Hyperchem package (Hyperchem, Inc., Gainsville, FL). They demonstrated that *p*-nitrobenzaldehyde **2f** (0.218) is more reactive than benzaldehyde **2d** (0.223).

Other studies reported that the reaction of lithium 2,2'-biphenolate with alcenyltrichlorosilanes leads to ß-allylic alcohols *via* pentacoordinated silicates intermediates [21]. Furthermore, Mall [22] showed that aluminum chloride catalyzed the isomerization of N-acylaziridines into oxazolines by means of tetracoordinated aluminates. Recently, we have reported that the *N*-acyl-2,2-dimethylaziridines are transformed in the presence of alumina, silica gel and acid activated clays into mixture of oxazolines, *N*-methallylamides and amidoalcohols *via* pentacoordinated silicate and tetracoordinated aluminate intermediates [17].

Two competitive ionic mechanisms could be proposed in order to explain the formation of dioxolane **3a-f**. The First step in this catalytic process represents the adsorption of the substrates **2a-f** on the active surface clay [23]. The formation of the coordinate bond between the Lewis acceptor sites (silicon and aluminum atoms) of clay HA and the oxygen atom of the carbonyl group of aldehyde **2** leads to the formation of pentacoordinated silicate **I** and tetracoordinated aluminate **II** intermediates. Then, ethylene glycol **1** attacks the carbonium ion of two intermediates **I** and **II** to give the corresponding zwitterions **IV** and **V**. The ring closure of these latter intermediates gives dioxolane **3** and generates the wet clay (Scheme 3, route a). Secondly, the obtaining of dioxolane **3** by acetalization of aldehyde **2** catalyzed by Bronsted acid sites located on the active surface of the protonated clay HA. These sites react with substrate **2** to form the carbonium ion **III**. The additition of ethylene glycol **1** on this intermediate **III** leads to dioxolane **3** *via* the oxonium ion **VI** (Scheme 3, route b).



Scheme 3. Mechanism proposed of synthesis of dioxolanes **3** from **2** and **1** catalyzed by clay HA.

These mechanisms are similar to that proposed for the reaction of acetalization of 1,2-diols and 1,3-diols with the carbonyl compounds which have been catalyzed by the Bronsted acids (HCl, H_2SO_4, TsOH, AcOH) and Lewis acids (SiO_2, BF_3), to give rise to the corresponding dioxolanes [24].

CONCLUSION

In this work, we have developed a novel synthesis method of 2-monosubstitued 1,3-dioxolanes from ethylene glycol and insatured aldehydes with satisfactory yields under optimal experimental conditions (Tunisian acid activated clay, under autogenously pressure and solvent-free) to meet demands of green chemistry. The NMR spectroscopic studies and the theoretical calculations are in good agreement with the experimental results of the acetalization reactions.

EXPERIMENTAL AND CALCULATION DETAILS

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 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 6-31G (d,p) were 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 raw clay:

200 g of crude clay are dispersed in 60 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:

30 g of raw clay are warmed in reflux in 300 mL of a solution of HCl (3 M) 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. The pH of the filtrate is 5.2. 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 aldehyde **2** and 50 mg of clay HA. The closed reactor is heated at 140 °C for 24 h under autogenously pressure. After cooling, clay is separated by filtration. 20 mL of distilled water was added to the crude to remove ethylene glycol **1**. The aqueous solution is extracted with ether (3 x 50 mL). The organic layers are collected then washed with 20 mL of distilled water. After drying ($MgSO_4$), the ether is evaporated under vacuum. The dioxolane **3** is then obtained.

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