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Synthesis of organic compounds by efficient solid catalysts based on silica and alumina

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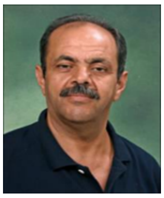

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Abstract

Heterogeneous catalysis by alumina, silica, clays, sulfuric acid adsorbed on silica, aluminum bisulfate, acid activated clays and cations pillared clays by has been studied to achieve new selective reactions in organic synthesis by the requirements of green chemistry. These catalysts are characterized with its interesting catalytic activity in a large number of heterocyclic and organic compounds synthesis reactions and can be recovered quantitatively and then used in other reactions; as a result, the cost of preparing the chemical is low. As in the case of dioxolanes formation, cleavage of these heterocyclic compounds requires wet acid catalysis.

1. Introduction

The acetalization reaction is well known as a synthesis procedure for the protection of carbonyl groups in multi-stapes chemical synthesis [1-3]. We are interested in 1,3-dioxolanes which are part of the skeletons of a large variety of organic and biological molecules which gives a very interesting applications in the biological and industrial fields [4-6].

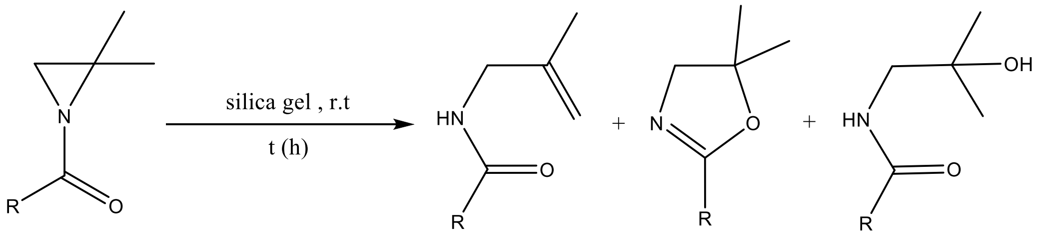
The synthesis of these heterocycles requires the presence of solid catalysts like alumina, silica and clays. These catalysts are non-polluting for the environment and easily separable from the reaction products by simple filtration, which can be recovered quantitatively and then used in other reactions, as a result, the cost of preparing the chemical is low [7-9]. Most of these methods described so far are long procedures involving high amounts of catalysts and substrates at high temperatures [10-12].

For economic and ecological reasons, organic chemists have faced a growing demand to optimize their synthesis methods in order to have the desired product with high yield and selectivity through an efficient and environmentally acceptable process [13-15].

2. Results and discussion

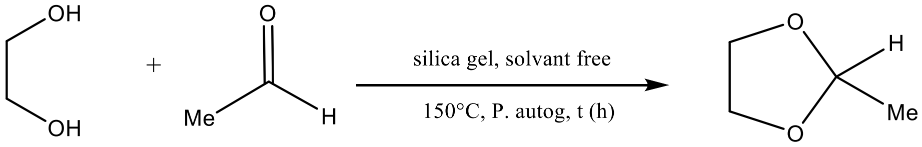
2.1 Silica gel

Silica is characterized with its interesting catalytic activity in a large number of organic synthesis reactions. Currently, several reactions can be performed cleanly and rapidly under moderate conditions using reagents that have previously been adsorbed on inorganic supports. This solid catalyst has been one of the most widely used inorganic supports in organic synthesis [16-18]. Silica gel, behaving as Lewis acid, reacted with N-acyl-2,2-dimethylaziridines to lead to allylamides, oxazolines and amidoalcohols [19].



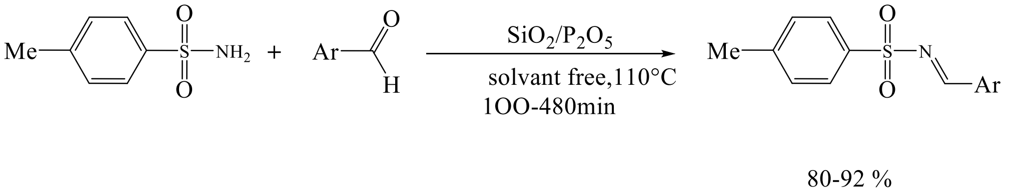
Scheme 1. Action of silica gel on N-acyl-2,2-dimethylaziridines.

The heating of ethylene glycol in a 150 °C autoclave for 24 hours, under autogenic pressure and in the presence of silica gel promotes the formation of in situ acetaldehyde which is trapped by the glycol ethylene present in the heterogeneous environment to lead to 2-methyl-1,3-dioxolane [20].



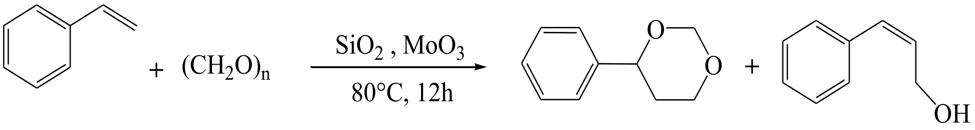
Scheme 2. Conversions of ethylene glycol using silica.

Some researchers have also used the silica gel supported by sulfuric acid as an effective catalyst in acid-catalyzed reactions such as alcohol dehydration and the preparation and hydrolysis of 1,3-dioxolanes. Hasaninejad et al carried out also the condensation reaction of sulfonamides with aromatic aldehyde in the presence of phosphoric oxide supported on silica [21].



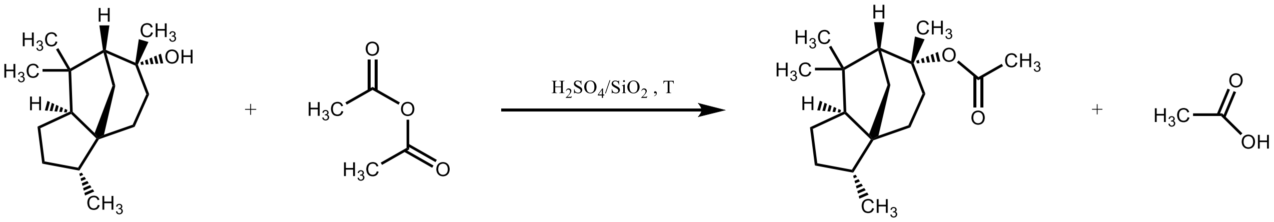
Scheme 3. Condensation of sulfonamides with aromatic aldehydes catalyzed by SiO_2/P_2O_5.

Molybdenum oxide supported on silica is a well known solid used as acid solid catalyst, it has both high Lewis and Bronsted acidities, and considered as a very effective catalyst for the synthesis of 1,3-dioxanes [22].



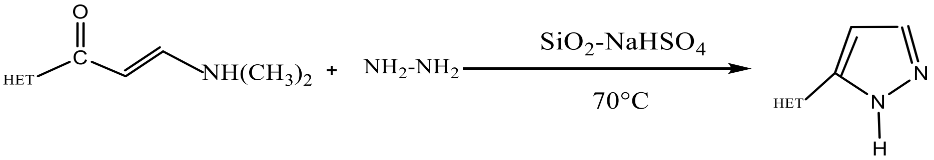
Scheme 4. Paraformaldehyde action on styrene in the presence of SiO_2/MoO_3.

Researchers used acetic anhydride to acetylate the compound (+) cedrol in the presence of a catalytic amount of SiO_2/H_2SO_4 under solvent-free conditions. Silica sulfuric acid is used as a heterogeneous catalyst in effective and reusable solution for the preparation of 2H indolo [2,1-b] phthalazinetrione, which is effective for acetylation of alcohol in solution and solvent-free reagents [23].



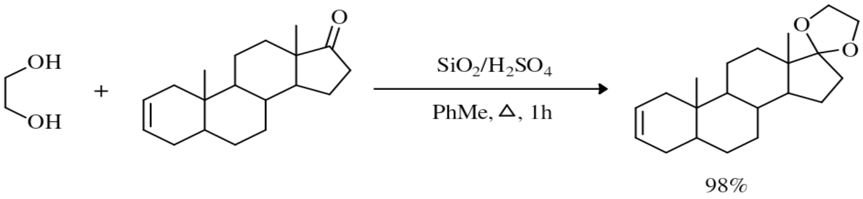
Scheme 5. Acetylation of the compound (+) – cedrol in the presence of silica/H_2SO_4.

Siddiqui reported that sulfuric acid adsorbed on silica gel is a good catalyst in the reactivity of β-enamineone heterocycles. Thus, this author uses the sodium sulfate supported on silica ($NaHSO_4$-SiO_2) as a heterogeneous catalyst for the synthesis of pyrazole and pyrannyl (pyridine derivatives) [24].



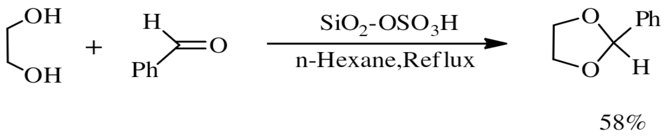
Scheme 6. Reactivity of β-enaminenes to hydrazine in the presence of $SiO_2/NaHSO_4$.

Sulfuric acid adsorbed on silica gel is a good catalyst for the condensation of ketosteroids with ethylene glycol, while metal sulfates adsorbed on the silica gel in microwave and without solvent, promote the protection of aromatic and aliphatic aldehydes in corresponding 1,3-dioxolanes [25].



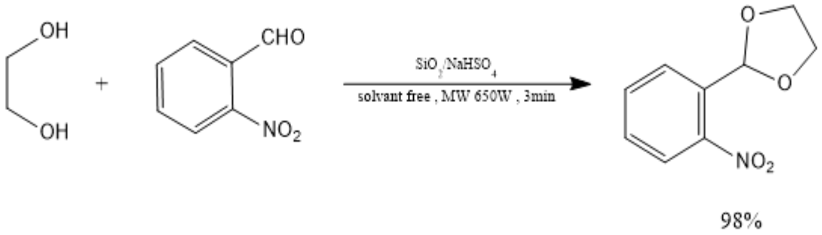
Scheme 7. Ketosteroid acetalization catalyzed by silica / H_2SO_4.

A wide range acetalization reaction of carbonyl compounds by diols under green environmental conditions results in dioxolanes with excellent yields. On the other hand, Kropp used different acids (AcOH, CH_3SO_3H or H_3PO_4) adsorbed on the silica gel for the hydrogenation of alkenes and alkynes, the cyclization of diestères and the cycloaddition of alcohols [26].



Scheme 8. Benzaldehyde acetalization in the presence of silica supported sulfuric acid.

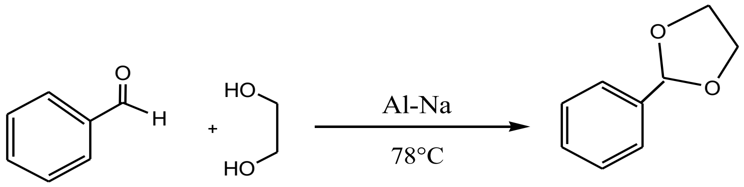
Several aliphatic, α,β-unsaturated and heterocyclic compounds have been selectively protected to give the corresponding products with high yields. Among the various metallic sulfates supported on silica gel we mention: $Ce(SO_4)_2$, $MgSO_4$ and $NaHSO_4$. It is noted that $NaHSO_4$ proved to be the most effective for the acetalization of 2-nitrobenzaldehyde in the microwave [27].



Scheme 9. Reactivity of 2-nitrobenzaldehyde vis-à-vis silica/H_2SO_4 under miro-wave.

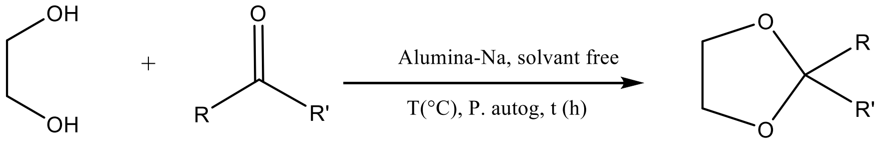
2.2 Alumina

Several reactions can be performed cleanly and quickly under moderate conditions using reagents that have been previously adsorbed to inorganic supports. Telalović succeeded in synthesizing tetrahedral aluminum that was stabilized by sodium as a counter-cation and then using it as a catalyst in the synthesis of benzaldehyde's 2-phenyl-1,3-dioxolane [28].



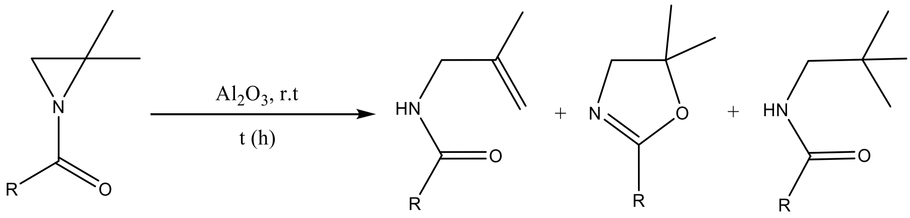
Scheme 10. Benzaldehyde Protection by ethylene glycol catalyzed with Al-Na.

A new strategies has been developed by organic chemists aiming to solvent-free organic synthesis. A sustainable conversion of ethylene glycol into dioxolanes using alumina showed yield of 40% within 24h [29].



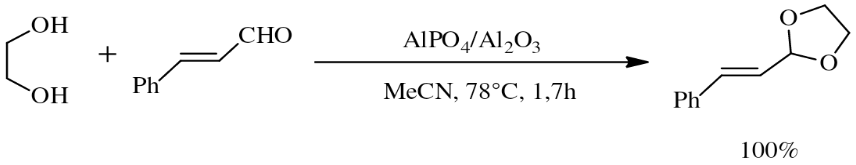
Scheme 11. Conversions of ethylene glycol using alumina.

Besbes et al verifiey the stability of N-benzoylaziridine on neutral alumina carriered out at room temperature and reflux transform N-acyl-2,2-dimethylaziridines into a mixture of N-methallylamides, oxazolines and amidoalcohols [30].



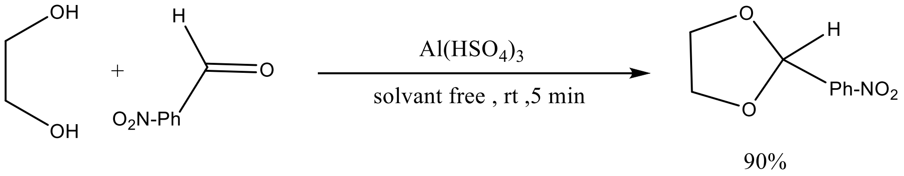
Scheme 12. Action of neutral alumina on N-acylaziridines.

The literature has described the usage of synthetic amorphous $AlPO_4$ and $AlPO_4$-Al_2O_3 as metal carrierd in alkene hydrogenation reactions. In addition, the external nature of these catalysts allows them to be used in several reactions such as Knoevenagel condensation in a dry medium [31].



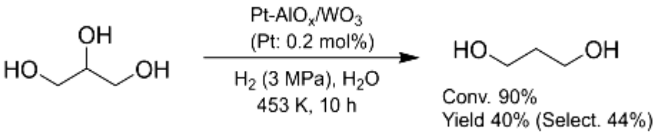
Scheme 13. Acetalization of α,β-unsaturated aldehydes in the presence of $AlPO_4$.

Aluminum bisulfate $Al(HSO_4)_3$ is a very stable and non-hygroscopic salt, it is considered as a solid material insoluble in most organic solvents. The acetalization of arylaldehydes is successful in the presence of this catalyst and the results are very interesting [32].



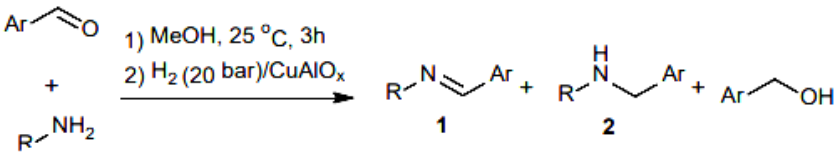
Scheme 14. Acetalization of p-nitrobenzaldehyde in the presence of $Al(HSO_4)_3$.

Many heterogeneous catalytic systems such as (Pt-AlOx/WO_3) consisting of platinum Nanoparticles (Pt NP) and aluminum oxides (AlOx) supported on tungsten trioxide (WO_3) were prepared by the co-impregnation method using an aqueous solution of $H_2[PtCl_6]$ and $Al(NO_3)_3$ with WO_3. These solid catalysts favored a 90% conversion and 40% efficiency to 1,3-PDO [33].



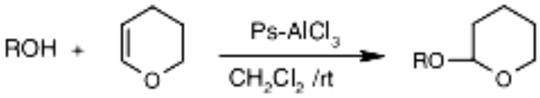
Scheme 15. Glycerol transformation into 1,3-propanediol presence of (Pt-AlOx/WO_3).

Nuzhdin et al have shown that mixed LDH-based Oxides Cu-Al are able to catalyze the N-methylation of p-anisidine with a high yield of N-methyl-p-anisidine which makes it possible to synthesize secondary amines with a yield of 98% [34].



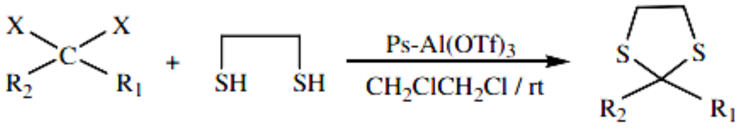
Scheme 16. Primary amines action on aromatic aldehydes with primary amines catalyzed by Cu-Al.

Bahman et al used Al-supported polystyrene $AlCl_3$, Ps-$AlCl_3$, as a catalyst for condensation, esterification and acetalization of alcohols. Ps-$AlCl_3$ was a good catalyst for the synthesis of thiiranes from epoxides for the highly chemoselective dithioacetalization of carbonyl compounds [35].



Scheme 17. Thiiranes synthesis from cyclohexenone.

The polymer catalyst obtained Ps-Al(OTf)3 is used as an effective agent as well as a highly chemioselective heterogeneous catalyst for the dithioacetallization of carbonyl compounds and the trans dithioacetallization of acetals [36].



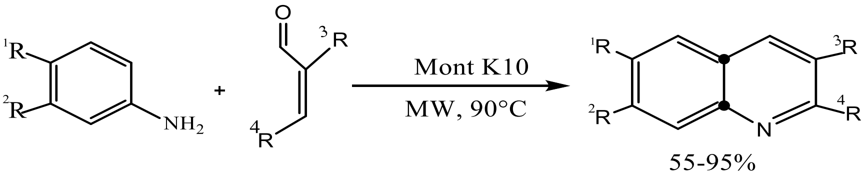
R_1, R_2 = Aryl, Alkyl, or H

X = OMe, OEt ; XX= O, -O$(CH_2)_3$O-, -O$(CH_2)_3$S-

Scheme 18. Dithioacetallization catalyzed by Ps-Al(OTf)3.

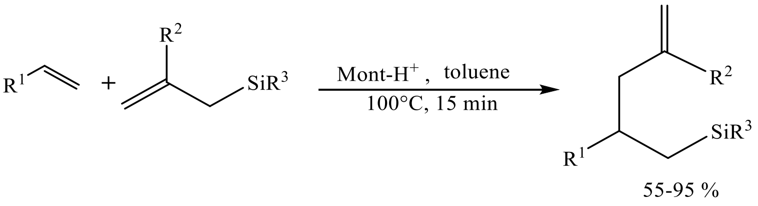
2.3 Clays and supported-clays

Clays have been widely used as a catalyst and support in several organic reactions [37, 38]. The reaction of amines with carbonyl compounds in the presence of montmorillonite K10 under microprobes leads to imines and isoquinolines [39].



Scheme 19. Amines addition on cinnamaldehyde in the presence of clay under microwave.

Acid-activated montmorillonite (smectite) is used in many reactions such as the dimerization of unsaturated fatty acids into dicarboxylic acids, the alkylation of phenols and also in the addition reaction [40].



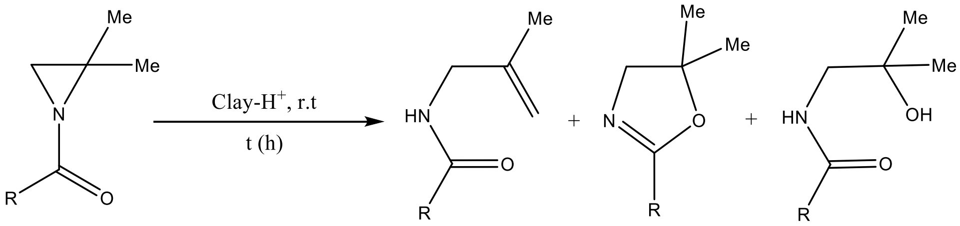
R_1 = 4-Cl-C_6H_4, 4-Br-C_6H_4, 4-F-C_6H_4, n-C_4H_9, n-C_6H_{13}

R^2 = H, CH_3

R^3 = CH_3, C_2H_5

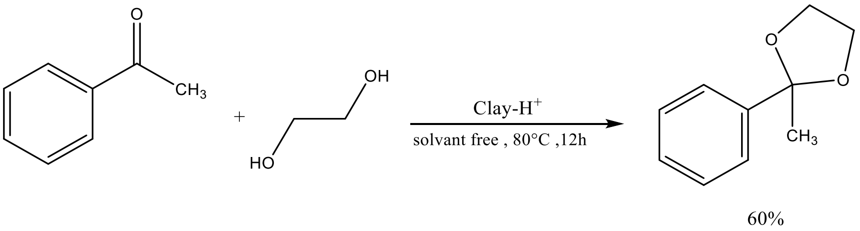
Scheme 20. Allylsilanes addition on aromatic and aliphatic alkenes.

Tunisian acid activated clays have been used for the rearrangement of N-acyl-2,2-dimethylaziridines into a mixture of N-methallylamides, oxazolines and amidoalcohols at room temperature for three days. The results shows that the yields of these products depend strongly on the nature of acyl group carried by nitrogen of aziridine cycle [41, 42].



Scheme 21. Rearrangement of N-acyl-2,2-dimethylaziridines using acid clay activated.

Heterogeneous acid catalyst based on a natural resource, Tunisian clay (clay-H$^+$), has been used in the reaction between acetophenone and ethylene glycol shows high yield of 66% at 80 °C [43].

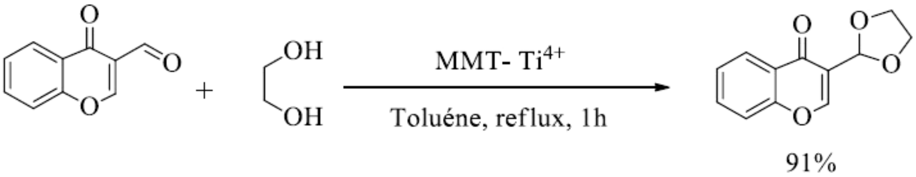


Scheme 22. Acetalization of acetophenone using clay-H$^+$.

The synthesis of cyclic cetals from carbonyl compounds (aldehydes and ketones) by diols and alcohols plays a key role in protecting and deactivating carbonyl compounds. Long before, this reaction is carried out in toxic and polluting organic solvents (HCl, H_2SO_4, AcOH and APTS). The acetalization of carbonyl compounds with methanol was carried out in the presence of montmorillonites exchanged by M^{n+} cations. Linear ketones and aldehydes were partially converted under these conditions. The order of the catalytic efficiency of montmorillonite/ M^{n+} is:

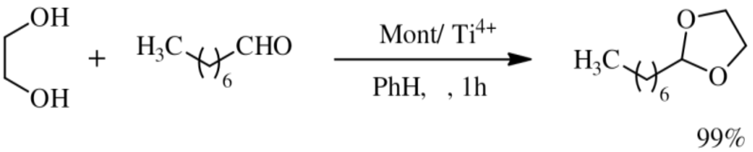
Montmorillonite/ Ce^{3+} > Fe^{3+}, Al^{3+}, Zr^{4+}>> Zn^{2+}, Na^+, H^+

Various works have been established on the use of clays as an alternative to these conventional homogeneous acids and which meets the principles of green chemistry. We cite the acetalization of aromatic aldehydes catalyzed by titanium-pillared clay with a yield of 91% [44].



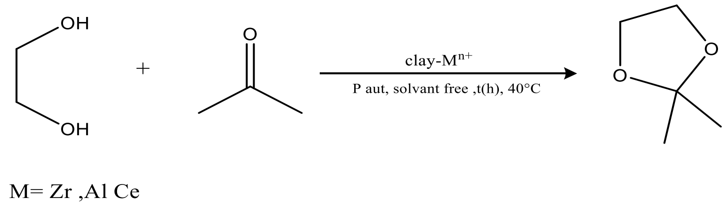
Scheme 23. Aldehyde protection of in the presence of montmorillonite decked with titanium.

Titanium-pillared clays are very strong acid catalysts used for selective acetalization reactions of carbonyl compounds by ethylene glycol [45]. This type of catalyst is effective with congested ketones aldehydes, dioxolane is formed with a yield of 99%.



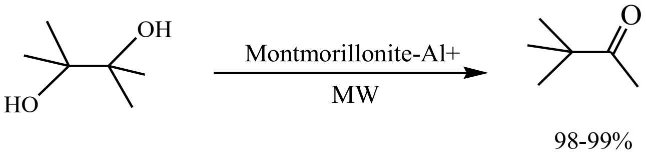
Scheme 24. Acetalization in the presence of montmorillonite/Ti^{4+}.

The use of zirconium-pillared clay (Zr-G or Al-Zr-G), has been applied for the preparation Ce, Al and Zr bridged clays and used as heterogeneous catalysts for the preparation of 2,2-dimethyl-1,3-dioxolane under mild conditions [46].



Scheme 25. Synthesis of 2,2-dimethyl-1,3-dioxolane in the presence of pillared clays.

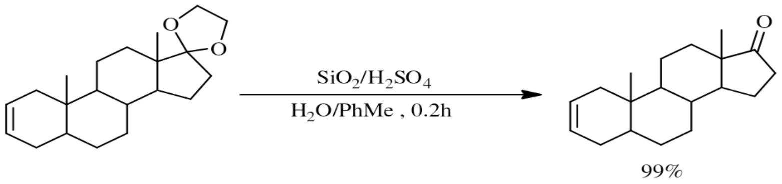
Montmorillonites exchanged by cations are also effective catalysts. Indeed, the montmorillonites exchanged by Fe and Co are used for the protonation of several organic species while the montmorillonites exchanged by Al and Cr are used in lactonization reactions and in the pinacolic rearrangement [47].



Scheme 26. Pinacolic rearrangement reaction catalyzed by montmorillonites exchanged by Al and Cr

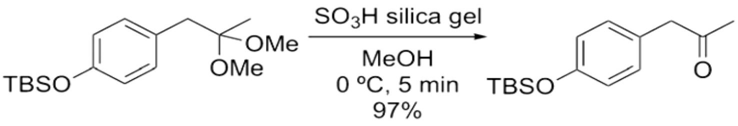
2.4 Acetals deprotection

As in the case of acetal formation, cleavage requires acid catalysis. These heterocycles can only be hydrolyzed with an acid catalyst because they are stable in a basic medium [48-50]. The general methods of cleavage described in the literature are carried out in the presence of water or alcohol [51-53]. This method is incompatible for other functional groups in the molecule that are sensitive to acid hydrolysis.Several researches were then carried out using different heterogeneous catalysts. The opening of the dioxolane ring is carried out by sulfuric acid supported by silica gel [54].



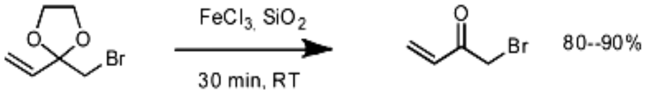
Scheme 27. Ketosteroid deprotection.

Selective deprotection of highly acid labile protecting groups in the presence of a TBS group remain intact at 0°C and selectivly convert dimethyl acetal to ketone in 5 minutes with hight yield 97% [55].



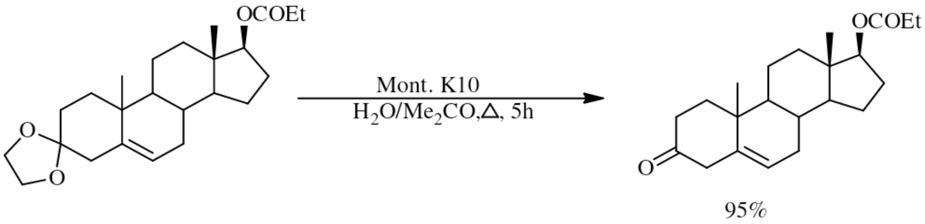
Scheme 28. Selective deprotection of dimethyl acetal in the presence of TBS group.

Method for acetal cleavage with iron(III) chloride on silica has been published [56]. This reagent is prepared by adding ferric chloride dissolved in acetone to silica. The method gives a high yield (80-90%) in 0.5 hours of the corresponding bromide unsaturated ketone.



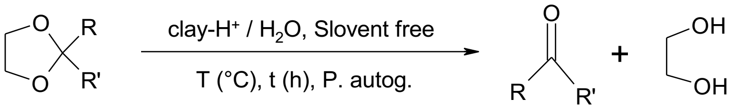
Scheme 29. Bromoacetal deprotected by $FeCl_3$ on dry silica.

Commercial montmorillonite K10 has been used for easy deacetalization reaction, but it should be noted that this reaction requires a large amount of this catalyst [57].



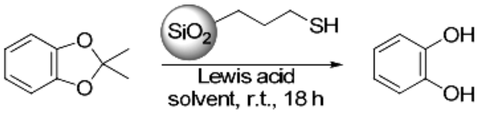
Scheme 30. Wet montmorillonite K10 Reactivity with dioxolanes.

Besbes showed that dioxolanes formed in situ from carbonyl compounds and ethylene glycol are unstable in the presence of acid-activated Tunisian clay and regenerate corresponding reagents [58].



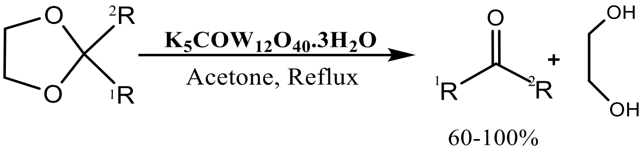
Scheme 31. Rearrangement of dioxolanes under Tunisian acid activated clay.

A practical and effective method developed for the deprotection of aliphatic acetals and their corresponding catechol or diol derivatives uses functionalized thiols on silica. The method is mild and gives a high yield (93%) with an excess of thiol [59].



Scheme 32. acetals cleavage by solid-supported thiol.

Other work also devoted to the cleavage of acetals by acid catalysis in the presence of $K_5CoW_{12}O_{40}\cdot 3H_2O$ and Mont.-Ti^{4+} [60].



Scheme 33. Dioxolane deprotection by a solid support.

Disclosure statement: *Conflict of Interest:* The authors declare that there are no conflicts of interest. *Compliance with Ethical Standards:* This article does not contain any studies involving human or animal subjects.

3. Conclusion

Environmental and economic considerations are driving an urgent need to rethink a commercially important process. In this context, heterogeneous catalysts plays a dramatic role; these catalysts are advantageous over homogeneous catalysts as they can be easily recovered from the reaction mixture.

References

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