

Research article

The First Example of Thia-Michael Addition Catalysed by Expanded Perlite

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Abstract

The expanded Perlite was used as new and efficient heterogeneous catalyst for Thia-Michael reaction between chalcones derivatives and mercaptans. Products of undesirable side reactions resulting from 1,2-addition, polymerisation and bis-addition are not observed. The work-up procedure is simplified by simple filtration with the use of catalyst. **Copyright © acascipub.com, all rights reserved.**

Keywords: Expanded Perlite, Thia-Michael reaction, Heterogeneous catalysis, Recyclable catalyst.

1. Introduction

Perlite is an amorphous volcanic glass that has relatively high water content, typically formed by the hydration of obsidian [1]. It occurs naturally and has the unusual property of greatly expanding when heated sufficiently. In Morocco, the largest deposit of perlite is the mines of Jbel Tidiennit located 17 km SW of Nador and possesses

about 38×10^6 tons of reserves of perlite [2]. With the object of investigating the economical upgrading of Moroccan natural resources [3] for example the Perlite, recently the Moroccan Authors have directed our interest to feasibility of adsorption of chromium (III) onto expanded Perlite [4].

Thia-Michael addition reaction [5] is one of the most fundamental C-S bond-forming reactions in the synthesis of β -mercapto carbonyl derivatives which have valuable synthetic scaffolds for biological, medicinal and synthetic organic chemists [6]. Conjugate addition of sulfur-centered nucleophiles to α,β -unsaturated carbonyls such as chalcones serves a powerful synthetic method in this area of sulfur chemistry [7]. Traditionally, the 1,4-addition of thiols is catalyzed by strong bases [8] such as alkali metal alkoxides, hydroxides, and amines. However the use of either strongly acidic or basic conditions frequently leads to the formation of undesirable side products owing to competing reactions, such as polymerization, self-condensation and rearrangements. Nevertheless, advantages of the heterogeneous synthesis [9] are very interesting; reactions take place in simple and mild conditions [10]. The products obtained are generally pure and separated easily [11].

As part of our program aimed at developing new selective and preparatively useful methodologies based on the use of solid catalysts as promoters of fine chemicals preparation, we found that the expanded Perlite is a good catalyst, able to promote the Michael addition of chalcones as acceptors with various mercaptans in mild reaction condition.

2. Materials and Method

2.1. Chemicals and Instrumentation

All chemicals used in this study were of reagent analytical grade. For solvents were used without further purification. The crude product was purified by recrystallization or by distillation under vacuum. And characterised by their ^1H NMR, ^{13}C NMR (NMR spectra were recorded on a Bruker ARX 300 spectrometer), IR spectrometry (FTIR spectra were recorded on an ATI Mattson-Genesis Series spectrophotometer using the KBr disc method) and melting point.

The X-ray fluorescence analysis was performed on a dispersion wavelength spectrometer SRS 200. The particle size of the expanded Perlite was measured using Mastersizer X (Malvern Instruments). The specific surface area was determined by BET Krypton adsorption method.

ESCA measurement were performed on VSW model HA 150 electron spectrometer, employing unmonochromatized $\text{AlK}\alpha$ (1486.6 eV) and $\text{MgK}\alpha$ (1253.6 eV) sources of photons, the pressure in the analytical chamber being in the low 10^{-7} Pa rang. The survey scans were recorded using fixed pass energy of 90 eV, while narrow scan spectra of the C_{1s} , O_{1s} , Si_{2p} and Al_{2p} levels were recorded using a fixed pass energy of 22 eV.

2.2. Preparation and Characteristics of expanded Perlite

The unexpanded Perlite samples were obtained from Jbel Tidiennit Perlite mines locates in Nador, Morocco. The Perlite was expanded in the Laboratory of the Office of Research and Mineral Participation. Perlite is an inert glassy volcanic rhyolitic rock which will expand when quickly heated to above 870°C . It expands up to 20 times its original volume.

The X-ray fluorescence analysis expanded Perlite shows that it is essentially amorphous natural alumino-silicate of white colour. The chemical composition of the expanded Perlite used in this study is summarised in table 1.

Table 1: Chemical analysis of Expanded Perlite

Constituent	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	P ₂ O ₅	TiO ₂	CaO	MgO	MnO	K ₂ O	Na ₂ O
Percentage (%)	75.22	13.08	01.83	00.02	00.13	01.43	00.10	00.06	04.95	03.00

However, XPS analysis of the extreme surface shows considerable enrichment in aluminium species (Si/Al= 4.65) compared to X-ray fluorescence results where atomic ratio of Si/Al =13. The only contaminant detected by XPS on the surface of expanded Perlite was carbon. The percentage and binding energy of elements presented at the expanded Perlite surface are summarised in table 2.

Table 2: Binding energy and Percentage of elements present in the surface of Expanded Perlite.

Constituent	Si _{2p}	O _{1s}	Na _{1s}	C _{1s}	K _{2p}	Al _{2p}
Binding Energy	0102.68	0532.00	1072.48	0284.60	0293.36	0073.92
Percentage (%)	23.7	55.9	06.1	07.0	02.3	05.1

The specific surface area of expanded Perlite is 1.726 m²/g and the particle size for this solid state ranged between 7.0 and 65.7 μm, 50% were 30.3 μm.

2.3. General Procedure

To a flask containing an equimolar mixture (1 mmol) of Michael donors **2** and Michael acceptors **1** in methanol (1.5 ml), the expanded Perlite (0.1 g) was added and the mixture was stirred at room temperature until completion of the reaction, as monitored by thin layer chromatography (Figure 1).

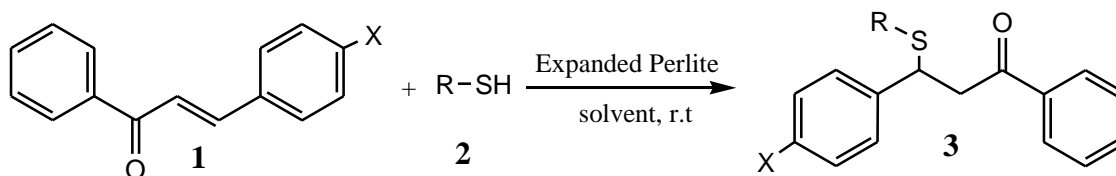


Figure 1: Thia-Michael addition catalyzed by expanded Perlite.

The catalyst was filtered, washed with dichloromethane and the filtrate was concentrated under reduced pressure. The crude product was purified by recrystallization. The product was analysed by ¹H, ¹³C NMR and IR spectrometry.

3. Results and discussion

We describe here an efficient method for Michael reaction catalysed by the expanded Perlite between chalcone **1** derivatives and mercaptans **2**, at room temperature, in methanolic solution.

The conjugate addition of thiophenol with chalcone in methanolic solution has been used as model reaction to study the expanded Perlite. Firstly, we investigated the use of calcinations temperatures for natural Perlite. Treatment at 100, 200 and 400°C led to catalysts with poor activities, but the use of the expanded Perlite calcined at 800°C led to

catalyst with high activity. This result of thermal treatment show that the Perlite proven to be potential candidate for heterogeneous catalyst.

Various solvents were tested. Thus, after 25 min of reaction the yields obtained of product **3a** are in presence of methanol (93%). In the cases of hexane, THF, dichloromethane, or butanol, no product **3a** was observed under the reaction conditions only the starting material was isolated. Thus, methanol was chosen as a solvent for further study. This result confirms the crucial role played by the solvent used to carry out the reaction.

Thereafter, we carried out the Michael addition of chalcones as acceptors with various mercaptans such as thiophenol, ethyl thioglycolate and 2-aminothiophenol catalysed by the expanded Perlite calcined at 800°C (100 mg) in the presence of methanol (1.5 ml) at room temperature (Table 3).

Table 3: Thia-Michael addition catalyzed by Expanded Perlite

Products	X	R	Yield % (time min)
3a	H	-Ph	93 (25)
3b	H	-2-NH ₂ -Ph	91 (05)
3c	H	-CH ₂ -CO ₂ -Et	74 (60)
3d	<i>p</i> -NO ₂	-Ph	93 (02)
3e	<i>p</i> -NO ₂	-2-NH ₂ -Ph	91 (02)
3f	<i>p</i> -NO ₂	-CH ₂ -CO ₂ -Et	88 (30)
3g	<i>p</i> -Cl	-Ph	91 (03)
3h	<i>p</i> -Cl	-2-NH ₂ -Ph	96 (02)
3i	<i>p</i> -Cl	-CH ₂ -CO ₂ -Et	86 (30)
3j	<i>p</i> -Me	-Ph	93 (50)
3k	<i>p</i> -Me	-2-NH ₂ -Ph	91 (05)
3l	<i>p</i> -Me	-CH ₂ -CO ₂ -Et	62 (60)
3m	<i>p</i> -OMe	-Ph	95 (225)
3n	<i>p</i> -OMe	-2-NH ₂ -Ph	92 (10)
3o	<i>p</i> -OMe	-CH ₂ -CO ₂ -Et	59 (90)

All products were isolated, purified, and analysed by ¹H, ¹³C NMR and IR. Products of undesirable side reactions resulting from 1,2 addition, polymerization and bis-addition are not observed.

The use of the expanded Perlite as heterogeneous catalyst for Michael reaction has allowed the isolation of products **3** rapidly and with good yields (74% to 96%), except for products (**3l**, **3o**).

The results observed with different Michael acceptors shown that the presence of an electron-donors group (OMe, CH₃) decreases their activity (**3l**, **3o**, **3n**) whereas the electron-acceptors group (NO₂, Cl) increases the activity of the Michael acceptors.

Indeed, we estimate that the surface of the expanded Perlite presents certainly multicycatalytic active sites. The basic sites enhance the donors (Thiol) nucleophilicity (Figure 2).

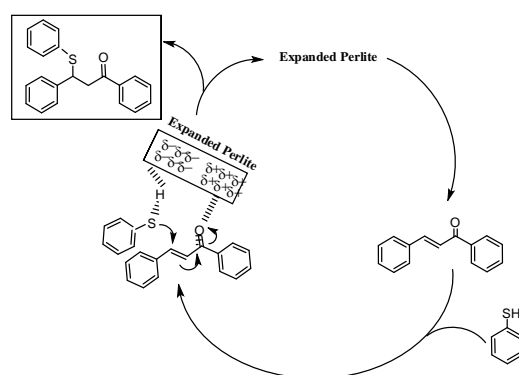


Figure 2: Mechanism of heterogeneous catalysis using Expanded Perlite

The acidic sites probably increase the enone (Chalcone) moiety polarization. Consequently, the carbon-sulfur bond formation is accelerated and the sulfanyl product is obtained by the transfer of proton.

In order to test their possible synthetic application, ketone **3a** was converted to oxime **4a** catalyzed by the Expanded Perlite. The oxime was subjected to the reaction by thionyl chloride and the chemoselective Beckmann rearrangement gave the anilide of 3,*N*-Diphenylsulfanyl-propan-1-one **5a**. Its alcoholysis furnished the corresponding ethyl ester **6a**. While compound **6a** is a direct precursor of β -thio acid **7a** (Figure 3).

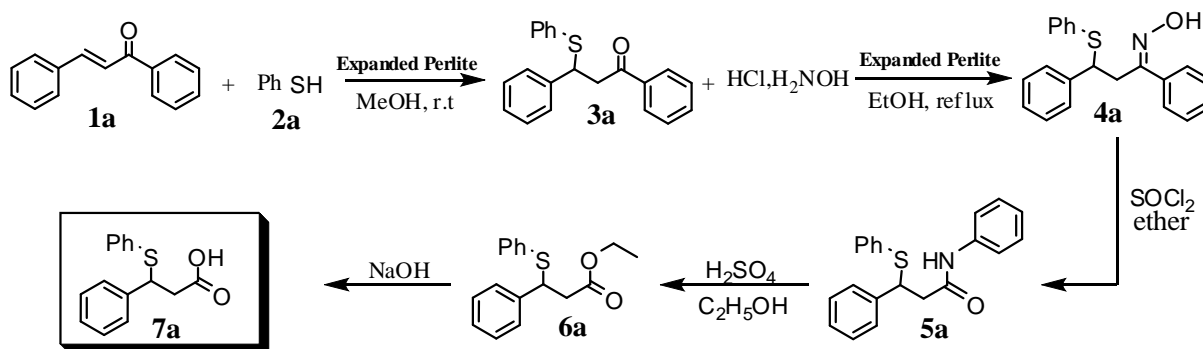


Figure 3: A simple route to synthesis of β -thio acid

We next investigated the stability of the catalyst in order to recycle it. The used and recovered expanded Perlite has been shown to be reusable after drying at 150 °C in vacuum, and more efficiently after washing with acetone followed by calcinations at 800 °C. In the last case, the catalyst can be recovered and reused at least five times without appreciable loss of activity.

4. Conclusion

The expanded Perlite catalyst applied in this study demonstrated good catalytic performance in conjugation addition between chalcone derivatives and mercaptans, and the separation of the catalyst is easy by simple filtration. This new solid base catalyst becomes then a practical alternative to soluble bases.

Acknowledgements

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