Tungstosilicic acid (H₄SiW₁₂O₄₀) Have Efficient Catalysts for Synthesis of 2,3-Dihydroxynaphthoquinone from Lawsone

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Abstract: The Thiele–Winter reaction is of interest for synthesis of tetracetoxyaromatic precursors of hydroxynaphthoquinones. Solid acids such as Tungstosilicic acid (H₄SiW₁₂O₄₀) have an efficient catalyst in acetoxylation reaction of naphtoquinones without the use of organic solvent at room temperature. 1,2,3,4-Tetrahydroxynaphthalene was easily oxidized at room temperature in 2,3-Dihydroxynaphthoquinone by using (Pc[Co]/K₁₀) and air (1 atm). We have also tested this type of reaction in 2-hydroxynaphtoquinone (Lawsone). Many naphtoquinones are natural products with interesting biological properties.

I. Introduction

The founding principles of green chemistry are mainly based on:
• The removal, if possible, of pollutant solvents that do not respect the environment. Nowadays, the use of inorganic solid acid catalysts in dry reactions (without organic solvent) offers many possibilities in the field of organic synthesis. Indeed they provide a simplification of the experimental protocols, easy recycling, and thereby easy protection of the environment.
• The improvement in the energy efficiency that beneficially affects the economy and the environment that must be considered and should be minimized by the development of synthetic methods at room temperature conditions.

Our attention has focused on the use of metallic phthalocyanines supported in the oxidative reactions of naphthotriols prepared from the
Thiele–Winter reaction in order to synthesize hydroxynaphthoquinone natural products having antibiotic properties. The acetoxylation reaction of Lawsone with acetic anhydride (CH₃CO)₂O catalyzed by sulfuric acid H₂SO₄ [11, 12] (H₀ = -11.94), at room temperature is slow with low yields especially in the presence of substituents on the naphthoquinone as electron donors. Sulfuric acid (H₂SO₄) was replaced by chlorozincique acid [13] and tetrafluoroboric acid [1] with low yields. To overcome this problem where the acidity of the medium thus protonation of the 2-hydroxynaphthoquinone is the decisive step, we opted for the use of solid super acid as heterogeneous conditions in the heteropolyacid: H₃SiW₁₂O₄₀. In our work we are particularly interested in the synthesis of 2,3-dihydroxy-1,4-naphthoquinone (3). Transformation of lawsone into tetracetoxy (2) by the Thiele–Winter reaction. The saponification of (2) followed by catalytic oxidation in situ of naphthotriols is shown in (Scheme 1).

![Scheme 1. Synthesis of 3 from Lawsone](image_url)

II. Experimental

II.1. Materials

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). The IR spectra were recorded as KBr pellets on Perkin Elmer 16 PC FT-IR spectrometer. UV–visible spectra (λmax log(ε)) were obtained with spectrophotometer Perkin-Elmer Landa 15. Microwave irradiation was carried out with a commercial microwave oven (Toshiba ER 7620) at 2,450 MHz, Mass spectra were carried out on analytical grinder A 10 of Janke and Kofler hot apparatus and are uncorrected. Proton NMR spectra (PMR) were determined on Brucker Ac 250 (250 MHz, CDCl₃, Me₄Si). The IR spectra were recorded as KBr pellets on Perkin Elmer 16 PC FT-IR spectrometer. UV–visible spectra (λmax log(ε)) were obtained with spectrophotometer Perkin-Elmer Landa 15.

II.2. Methods

II.2.1 Spectroscopic characterization of lawsone (2-Hydroxy-1,4-naphthoquinone): Orange solid, yield: 79 %, m.p: 194 °C, UV–visible λmax log(ε) (dioxane/H₂O) nm: 276.3 (4.48), 334.3 (3.28); IR (KBr) cm⁻¹: 3166 (v OH), 1676 (v C = O), 1592, 1170, 874, 536; ¹H NMR (CDCl₃): δ 6.37 (s, 1H, H arom); 7.26 (s, 1H, H arom.); 7.25-8.14 (m, 4H, H arom); C₁₀H₈O₃, calcd: H, 3.47 %; C, 68.97 %; found: H, 3.53 %; C, 68.92 %;

II.2.2 Phthalocyanine(Co) Supported on K10 (1)

a) Preparation of Montmorillonite K10 Exchange by Co²⁺

In a 250 ml flask, the Montmorillonite K10 (20 g) was added to a solution of metallic salt CoCl₂ (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 Co²⁺ was washed with methanol and recentrifuged. The solid was dried for 24 h in vacuum then finely ground. The final product was a clear beige color.

b) Phthalocyanine Intercalated in the Montmorillonite K10

A solution of phthalonitrile (20 mmol; 2.56 g) dissolved in 20 ml of dichloromethane was added to the solid Montmorillonite K10 (5 g) exchanged with some metallic cations (Co²⁺). After contact for 2 h, the remaining liquid was evaporated under reduced pressure. The activation of the solid under microwave irradiation (MO): p = power, t = time of irradiation) was carried out in a resonance cavity. After cooling, the solid was successively washed with water, acetonitrile (20 ml), and then with dichloromethane (20 ml). The solid was dried under reduced pressure and the extracted with acetoniitrile as a solvent using a Soxhlet for 8 h. Catalysts were characterized by FT-IR; electronic spectra of metatalated phthalocyanine intercalated into Montmorillonite were very close to those observed with pure metatalated phthalocyanine, but the bands were shifted. (Pc[Co] Supported on K10) (1): microwaves irradiation Resonance Cavity. (p = 630 W, t = 10 min); Purple solid, m.p > 300 °C C₉H₈CoN₄; yields: 85 %, UV-visible λmax log(ε) / (1-chloronaphthalene) nm: 669.5 (4.42); 642.1 (3.88); 604.2 (3.78); 580.1 (3.22); IR (KBr) cm⁻¹: 1636, 1522, 1400, 1044, 870, 796, 756, 532, 525, 466.

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II.2.3 Acetoxylation Reaction Under Heterogeneous Conditions (Solid Acids)

In a typical experiment, 10 mmol of Lawsone were dissolved in acetic anhydride (0.2 mol; 21.64 g). One gram of catalyst (H₂SiW₁₂O₄₀) was added and the mixture was stirred at room temperature. After 48 h, the products were separated by chromatography on a silica column eluted successfully with ethyl acetate/cyclohexane (10/90). The different fractions gave, respectively, a yellow solid (unreacted quinone) and a beige solid (1,2,3,4-tetracetoxynaphthalene) (2). It must be noted that traces of products of diacetylation could be detected by thin-layer chromatography (TLC).

1,2,3,4-Tetracetoxynaphthalene (2): Beige solid, yield 66 %, m.p: 149 °C, C₂₄H₁₃O₈; IR (KBr) cm⁻¹: 3012 (v C=O), 1678 (v CH arom.), 1760 (v OCOCH₃); 1'H NMR (CDCl₃): δ 2.39 (s, 6H, OCOCH₃); 7.46–8.14 (m, 4H, H arom.).

We have studied this reaction with strong acids. Chlorosulfonique acid (Ho = 13.80) [14-16] led to the desired product. The reaction with solid super acids shows a high Brønsted acidity. Heteropolyacids (HPAs also called polyoxometalates) are catalysts of very great interest [17, 18]. The display has a very high Brønsted acidity close to super acids. We decided to test three heteropolyacids H₃PW₁₂O₄₀ (PW), H₂SiW₁₂O₄₀ (SiW), and H₃PMO₁₂O₄₀ (PMO). The (SiW) provided the product with a yield of 66 % whereas a yield of 61 % was achieved with the (PW). It has been noticed that the (SiW) appeared a better catalyst than the (PW). This could be because of the higher ratio of the number of protons in (SiW) [19].

We have noticed that no product (3) was obtained with the H₃PMO₁₂O₄₀ (PMO). The reaction medium color changed from green to deep blue, proving the reduction of PMO. The result with (PMO) is not surprising owing to its high redox potential resulting from the presence of the molybdenum atom. Results of acetoxylation of Lawsone by acetic anhydride obtained from different acids catalysts are reported in Table.1.

### Table 1. Acetoxylation of Lawsone at 20 °C

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Aspect</th>
<th>Hammet:</th>
<th>Experimental</th>
<th>M.p.(°C)</th>
<th>IR vester (cm⁻¹)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂SO₃H</td>
<td>Liquid</td>
<td>-13.80</td>
<td>20C, 20h</td>
<td>149</td>
<td>1772</td>
<td>54</td>
</tr>
<tr>
<td>H₃PW₁₂O₄₀</td>
<td>Solid</td>
<td>-13.6</td>
<td>20C, 48h</td>
<td>149</td>
<td>1768</td>
<td>61</td>
</tr>
<tr>
<td>H₃PMO₁₂O₄₀</td>
<td>Solid</td>
<td>-</td>
<td>20C, 48h</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂SiW₁₂O₄₀</td>
<td>Solid</td>
<td>-</td>
<td>20C, 48h</td>
<td>152</td>
<td>1760</td>
<td>66</td>
</tr>
</tbody>
</table>

The 1,2,3,4-tetracetoxynaphthalene (2) was easily transformed into (3) by saponification basic and oxidation with potassium hydroxide (KOH) in methanol (CH₃OH) in the presence of air at room temperature. The yield of 2,3-dihydroxy-1,4-naphthoquinone from (3) is good (91 %). The results obtained from the two-step sequence (tetracetoxyaromatic and saponification–oxidation in situ) are reported in Table.2.

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Table 2. Tungstosilicic acid (H₄SiW₁₂O₄₀) as catalyst for oxidation by molecular oxygen

<table>
<thead>
<tr>
<th>1) Thiele-Winter: tetracetoxyaromatic</th>
<th>2) [Saponification–oxidation] in situ</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="1" alt="Diagram 1" /></td>
<td><img src="2" alt="Diagram 2" /></td>
</tr>
</tbody>
</table>

Mechanism proposed:

IV. Conclusion

In conclusion it appears that heteropolyacids (H₄SiW₁₂O₄₀) can easily catalyze the Thiele-Winter reaction. This work represents the first example of catalysis of this reaction by solid acids. The sequence of the two steps (acetoxylation, saponification-oxidation) constitutes a new synthesis of 2,3-dihydroxynaphthoquinones from Lawson.
V. References


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