

金属酞菁催化脱羧合成 3,4-二烷氧基噻吩的简便方法

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摘要: 以金属酞菁为催化剂, 2,5-二羧酸-3,4-二烷氧基噻吩在水相中脱羧, 以较高的产率和纯度制得 3,4-二烷氧基噻吩, 避免了有机极性溶剂的使用, 催化剂重复使用 8 次仍表现出优异的催化性能. 另外, 通过简易的水蒸气蒸馏法即可分离出产物. 该方法具有环境友好、操作简易和反应时间短等优点, 是一种制备 3,4-二烷氧基噻吩的绿色方法.

关键词: 脱羧; 3,4-二烷氧基噻吩; 酞菁; 合成; 绿色化学

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A Facile Synthesis of 3,4-Dialkoxythiophenes through Decarboxylation Catalyzed by Metal Phthalocyanines

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Abstract: 3,4-Dialkoxythiophenes are electron rich and their polymers have a narrow energy gap, so they have recently attracted considerable attention in the field of organic semiconducting materials. However, the traditional synthetic approach suffers from some drawbacks, so the development of efficient methods for the synthesis of 3,4-dialkoxythiophenes is needed. A novel, efficient decarboxylation of 2,5-dicarboxy-3,4-dialkoxythiophenes was achieved in excellent yields (up to 95%) and purities using metal phthalocyanines in water, which avoids the use of organic polar solvents, and the recovered catalyst was successfully used in subsequent reactions. Furthermore, the desired products, 3,4-dialkoxythiophenes, were conveniently separated by steam distillation. This method has several advantages such as environmental friendliness, ease of manipulation, and a short reaction time. This environmentally friendly procedure represents a promising green route for the decarboxylation of these important compounds.

Key words: decarboxylation; 3,4-dialkoxythiophene; phthalocyanine; synthesis; green chemistry

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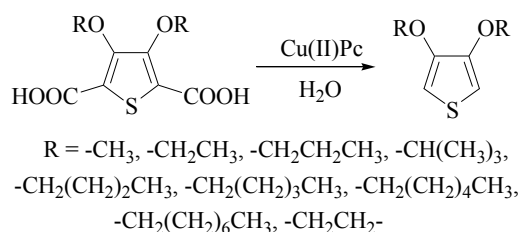
噻吩具有独特的电学、光学和氧化还原属性, 因而近年来在有机半导体材料领域受到很大关注, 已用于制作有机场效应晶体管、有机发光二极管和有机光伏电池等各种电子器件^[1-3]. 3,4-二烷氧基噻吩比未取代的噻吩具有更大的富电子属性, 因此, 此类

噻吩单元的聚合物的最高占据轨道和最低未占据轨道之间的能隙较窄^[4-7]. 其中以 3,4-乙撑二氧噻吩为单体的高分子化合物具有高电导率和化学稳定性、较窄的能隙以及良好的环境稳定性等特性, 因而成为最成功的导电高分子材料^[8-10]. 因此, 有必要发展

一种简便有效的合成 3,4-二烷氧基噻吩的方法^[11].

非均相催化剂具有催化效率高、易于存储与处理、分离与套用简便等特性. 金属酞菁 (MPcs) 有诸多优异的性质, 用途广泛^[12~14]. 由于它不溶于普通的有机溶剂, 通过过滤即可方便地从反应体系中分离出来. 因此, MPcs 作为众多反应的非均相催化剂表现出优异的催化效果^[15~21].

脱羧是生物过程和化学合成中一类重要反应^[22]. 然而, 传统的脱羧方法成本高, 产量低, 且在高温进行. 本文首次报道了 MPcs 在水相中催化脱羧制备 3,4-二烷氧基噻吩的方法, 见图式 1.



图式 1 Cu(II)Pc 催化脱羧制备 3,4-二烷氧基噻吩

Scheme 1. Synthesis of 3,4-dialkoxythiophenes through decarboxylation catalyzed by Cu(II)Pc.

早期研究^[23]表明, 2,5-二羧酸-3,4-乙撑二氧噻吩能在 Cu 或 Cu 盐的催化下, 在极性溶剂如喹啉、乙二醇和二甲基亚砷 (DMSO) 中, 回流反应较长时间 (一般 180 °C 以上), 可完成脱羧, 产率仅为 30%~60%. 另外, 产品和溶剂的沸点比较接近, 分离困难.

水具有廉价、环境友好、易于与反应物或者催化剂分离, 因而在水中进行有机反应备受关注^[24]. 另外, 水是一种可靠的极性溶剂, 因此在水中进行脱羧反应完全可能.

在水中, 以 Cu 为催化剂, 2,5-二羧酸-3,4-乙撑二氧噻吩进行脱羧反应, 没有得到目标产物. 基于温度可能是脱羧反应的一个关键要素, 在封管中, 我们将反应温度提升至 180 °C, 目标产物产率达到 90% (表 1, 实验 1).

从表 1 还可以看出, 除 Cu 以外, 其它铜系化合物也表现出较高的催化活性 (表 1, 实验 2~10). 进一步筛选实验表明, 铜酞菁和其它 MPcs 也能够催化脱羧反应 (表 1, 实验 12~18). 其中, MPcs 表现出更高的催化效率, 使得脱羧反应可在 100 °C 完成. 可见, 在常压水回流的条件下, MPcs 即可催化脱羧

表 1 不同金属化合物在水相中对于 2,5-二羧酸-3,4-乙撑二氧噻吩的催化脱羧

Table 1 Decarboxylation of 2,5-dicarboxy-3,4-ethylenedioxythiophene catalyzed by different metal compounds in water

Entry	Catalyst	Temperature (°C)	Time (h)	Yield ^a (%)
1	Cu	180	0.5	90
2	CuO	180	2	72
3	Cu ₂ O	180	2	83
4	CuCl ₂	180	2	65
5	CuBr ₂	180	2	68
6	CuCl	180	2	74
7	CuBr	180	2	75
8	CuI	180	2	80
9	CuSO ₄	180	4	57
10	Cu(OAc) ₂	180	2	83
11	Cu(II)Pc	100	1	95
12	Zn(II)Pc	100	1	92
13	Co(II)Pc	100	1	93
14	Ni(II)Pc	100	1	93
15	Mn(II)Pc	100	1	90
16	Mg(II)Pc	100	1	92
17	Fe(III)Pc	100	1	92
18	Ag(I)Pc	100	1	93
19	H ₂ Pc	100	4	0
20	Cu	100	4	0
21	—	100	24	0

^aAfter purification by steam distillation.

反应. 另外, 目标产物 3,4-乙撑二氧噻吩不溶于水, 因此通过简易水蒸气蒸馏即可分离出产物. 如表 2 所示, Cu(II)Pc 催化剂重复使用 8 次, 其活性没有降低, 表现出优异的重复使用性能.

表 2 Cu(II)Pc 的循环使用性能

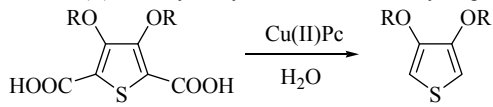
Table 2 Recycling of Cu(II)Pc in decarboxylation

Cycle	Time (h)	Yield ^a (%)
1	1	95
2	1	94
3	1	95
4	1	95
5	1	94
6	1	94
7	1	94
8	1	95

^aAfter purification by steam distillation.

为了考察 Cu(II)Pc 催化剂的适用范围, 以一系列 2,5-二羧酸-3,4-二烷氧基噻吩为底物进行了脱羧

表 3 Cu(II)Pc 催化合成 3,4-二烷氧基噻吩
Table 3 Cu(II)Pc catalyzed synthesis of 3,4-dialkoxythiophenes



Entry	R	Time (h)	Yield ^a (%)
1	-CH ₃	1	95
2	-CH ₂ CH ₃	1	95
3	-CH ₂ CH ₂ CH ₃	2	90
4	-CH(CH ₃) ₃	2	90
5	-CH ₂ (CH ₂) ₂ CH ₃	2	92
6	-CH ₂ (CH ₂) ₃ CH ₃	3	92
7	-CH ₂ (CH ₂) ₄ CH ₃	3	90
8	-CH ₂ (CH ₂) ₆ CH ₃	3	90

^aAfter purification by steam distillation.

反应, 结果见表 3. 可以看出, 不论长链烷氧基还是短链烷氧基取代的底物, 都以较高产率得到相应的 3,4-二烷氧基噻吩.

综上所述, 在水相中 MPcs 可催化 2,5-二羧酸-3,4-二烷氧基噻吩进行脱羧反应, 目标产物的产率和纯度较高, 且催化剂可重复使用, 避免了有机极性溶剂的使用, 通过简易水蒸气蒸馏即可实现产物分离. 该法具有环境友好、操作简易和反应时间短等优点, 是制备此类化合物的一种环境友好的方法.

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英 译 文

English Text

The electronic, optical, and redox properties of thiophenes have recently attracted considerable attention in the field of organic semiconducting materials for applications in electronic devices such as organic field-effect transistors, organic light-emitting diodes, and organic photovoltaics [1–3]. 3,4-Dialkoxythiophenes are more electron rich than unsubstituted thiophenes, and polymers based on such thiophene units are expected to show a narrow highest occupied molecular orbital/lowest unoccupied molecular orbital energy gap [4–7]. Among thiophene-based polymers, 3,4-ethylenedioxythiophene-based conjugated materials are the most successful conductive polymers because of their high electrical conductivity, chemical stability, low bandgap, and outstanding environmental stability [8–10]. The development of simple and efficient methods for the synthesis of 3,4-dialkoxythiophenes is therefore desirable [11].

Heterogeneous catalysts have received increasing attention because of their high catalytic efficiency, easy storage and handling, and facile separation and recycling. Metal phthalocyanines have many interesting properties and applications in several important technological fields [12–14]. They are insoluble in common organic solvents, so they can be easily separated from the reaction system by filtration. Metal phthalocyanines therefore show excellent performance as heterogeneous catalysts for a variety of organic reactions [15–21].

Decarboxylation reactions are important in a variety of biological processes as well as in synthesis [22]. However, traditional approaches suffer from drawbacks such as high costs, low yields, and high temperatures. In a continuation of our ongoing program on the development of efficient and environmentally benign protocols for the synthesis of 3,4-dialkoxythiophenes, we report here the first example of decarboxylation catalyzed by metal phthalocyanines in aqueous media (Scheme 1).

Early studies showed that the decarboxylation of 2,5-dicarboxy-3,4-ethylenedioxythiophenes could be catalyzed by copper or its salts in polar solvents such as quinoline, ethylene glycol, and dimethyl sulfoxide under reflux conditions (typically above 180 °C), but gave very poor yields (30%–60%) of 3,4-ethylenedioxythiophenes with long reaction times [23]. Also, the products and reaction media have similar boiling points, so isolation of the products is difficult.

As part of the development of green chemistry, organic reactions in aqueous media are an attractive alternative to the use of organic solvents because water is not only inexpensive and environmentally benign but is also easy to separate from organic reagents or catalysts [24]. In addition, water is a safe polar solvent, so we believed that these decarboxylation reactions could be performed in aqueous media.

We attempted the decarboxylation of 2,5-dicarboxy-3,4-ethylenedioxythiophenes catalyzed by copper in water, but no product was obtained. We further assumed that the temperature plays a key role in the decarboxylation reaction. To test this, in subsequent experiments, we raised the reaction temperature to 180 °C in a sealed tube, and obtained the desired products in excellent yields (up to 90%) (Table 1, entry 1).

In terms of resource conservation, the selection of simple and cost-effective catalysts is also an important topic. A preliminary study showed that copper was an effective catalyst for the decarboxylation in aqueous media, and other

copper compounds also showed good catalytic activity (Table 1, entries 2–10). During further catalyst screening, we found that copper phthalocyanines and other metal phthalocyanines could catalyze the reaction (Table 1, entries 11–18).

It is interesting that the metal phthalocyanine catalysts were more reactive than the other catalysts, giving good conversions at low temperatures (100 °C). The decarboxylation could be accomplished with ease in the presence of a catalytic amount of metal phthalocyanine in water at reflux conditions under atmospheric pressure. We observed oil droplets in the refluxing liquid and identified them as 3,4-ethylenedioxythiophenes, using gas chromatography/mass spectrometry. So, the products could be easily separated during the reaction, in good yields and purities, using a facile steam distillation. Furthermore, we found that the recovered catalyst could be successfully used more than eight times without loss of activity (Table 2).

To examine the scope of this decarboxylation reaction, various 2,5-dicarboxy-3,4-dialkoxythiophenes were examined as substrates. The results show that this reaction is equally facile with both long alkyl-chain and short alkyl-chain substituents, giving excellent yields of the corresponding 3,4-dialkoxythiophenes (Table 3).

In summary, we have developed an efficient decarboxylation of 2,5-dicarboxy-3,4-dialkoxythiophenes, in excellent yields and purities, using metal phthalocyanines as recyclable catalysts in water; this avoids the use of organic polar solvents. Furthermore, the desired products, 3,4-dialkoxythiophenes, were conveniently and easily separated by steam distillation. This method has several advantages such as environmental friendliness, ease of manipulation, and a short reaction time. This environmentally friendly procedure represents a promising green route for the decarboxylation of these important compounds.

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