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# Diprotodecarboxylation Reactions of 3,4-Dialkoxythiophene-2,5dicarboxylic Acids Mediated by Ag<sub>2</sub>CO<sub>3</sub> and Microwaves

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# DIPROTODECARBOXYLATION REACTIONS OF 3,4-DIALKOXYTHIOPHENE-2,5-DICARBOXYLIC ACIDS MEDIATED BY Ag<sub>2</sub>CO<sub>3</sub> AND MICROWAVES

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#### **GRAPHICAL ABSTRACT**



**Abstract** An efficient and rapid method is reported to obtain 3,4-dialkoxythiophenes from 3,4-dialkoxythiophene-2,5-dicarboxylic acids through a diprotodecarboxylation reaction with  $Ag_2CO_3/AcOH$  as a catalytic system and microwave heating in dimethylsulfoxide (DMSO) as solvent. This methodology lets us obtain for the first time good performance with thiophenes bearing strong electron-donating groups such as alkoxides. This methodology eliminates the usage of harmful quinoline as solvent, as well as the long reaction times typically used (12–18 h) to obtain the 3,4-dialkoxythiophenes. The reaction of 7 diacids showed good yields (60–89%) following 20 min of microwave heating in a temperature range of 120–150 °C.

[Supplementary materials are available for this article. Go to the publisher's online edition of Synthetic Communications<sup>®</sup> for the following free supplemental resource(s): Full experimental and spectral details.]

**Keywords** Ag<sub>2</sub>CO<sub>3</sub>; 3,4-dialkoxythiophene-2,5-dicarboxylic 3,4-dialkoxythiophenes; microwaves; protodecarboxylation

# INTRODUCTION

3,4-Dialkoxythiophenes are very important substances in the preparation of oligothiophenes and polythiophenes,<sup>[1]</sup> which have interesting electronic properties and find applications in electronic devices fabrication, as organic light-emitting diodes (OLEDs)<sup>[2a]</sup> and organic field-effect transistors (OFETs),<sup>[2b]</sup> electrochromic materials,<sup>[2c]</sup> biosensors,<sup>[2d]</sup> chemosensors,<sup>[2e]</sup> organic solar cells,<sup>[2r]</sup> etc. One of the

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best known and useful polythiophenes is polyethylenedioxythiophene (PEDOT). This polymer, when oxidized, has excellent conductivity (ca. 300 S/cm), is almost transparent, and shows great chemical stability to the environmental conditions.<sup>[3]</sup> In the classic synthesis of 3,4-dialkoxythiophenes such as 3,4-diethylendioxythiophene (EDOT, **2a**), the monomeric precursor requires a double aromatic protodecarboxylation reaction from a thiophene bearing two carboxyl groups in positions 2 and 5 (Scheme 1).<sup>[4]</sup> The main disadvantages of this reaction are the long reaction time (t > 12 h), high temperatures (T ≥ 150 °C) incompatible with some sensible functional groups attached to the thiophene ring,<sup>[5]</sup> and poor yields with electron-rich aromatic compounds as EDOT that do not react completely<sup>[6]</sup> (in the range of 45–64% from diacid).<sup>[4b]</sup> Generally, this process is carried out using a copper catalyst and the toxic and not environmentally friendly solvent quinoline.

In recent years more efficient protodecarboxylation methodologies for electronrich and electron-poor aromatic systems have been reported. Using the expensive palladium(II) trifluoroacetate as catalyst, it is possible to decarboxylate electron-rich aromatic systems. A method having broader scope was described by Gooßen,<sup>[7]</sup> who improved the protodecarboxylation of aromatic systems mediated by coopper catalyst with microwaves; unfortunately the inconvenient of using high temperatures (160–190 °C) and the moderate yields (62%) reported with thiophene derivatives makes its use unattractive with our starting materials. A third methodology, developed independently by Gooßen et al.<sup>[8a,8b]</sup> and Larrosa et al.,<sup>[8c,8d]</sup> uses Ag (I) as catalyst. In Larrosa's methodology, the temperature does not reach more than 120 °C and has been efficiently applied to some heteroatomic systems.<sup>[8d]</sup> Nevertheless, it has not been adapted to microwave heating and has been scarcely applied to some thiophene derivatives. Larrosa only reported transformations with



Scheme 1. Classical synthetic route to obtain 3,4-dialkoxythiophenes and poly-3,4-dialkoxythiophenes.

halogen-substituted thiophenes, and there are no reports of protodecarboxylations of thiophenes bearing strong electron-donating groups such as alkoxides. Thus, considering that as far as we know this procedure has never been used with the 3,4-dialkoxythiophene-2,5-dicarboxylic acids, in addition to the utility and value of the 3,4-dialcoxythiophenes, it was decided to attempt Larrosa's methodology with microwave heating for this thiophene family. Our intent was to eliminate the use of quinoline as the solvent and to reduce both the reaction time and temperature.

# DISCUSSION

In our initial studies, 3,4-diethylendioxithiophene-2,5-dicarboxylic acid (1a) was used as a model compound. The classical reaction with  $Cu_2Cr_2O_7$  and quinoline, but using microwave heating instead of an oil bath, was carried out at 150 °C only for comparative purposes (entry 1, Table 1). This reaction occurred in a 78% yield in only 15 min. This represents a substantial reduction in time and energy compared with conventional heating where 20 h reactions are required (see Scheme 1).<sup>[4]</sup> The

**Table 1.** Optimization of diprotodecarboxylation conditions<sup>a</sup>



Entry	Solvent	AcOH (mmol)	Catalyst (% mol)	T (°C)	Time (h)	Yield (%)
1	Quinoline	_	A (34)	$150^{b}$	0.25	78
2	DMSO	0.05	B (20)	120	16	54
3	DMSO	0.05	B (40)	120	16	35
4	DMSO	0.5	B (20)	120	16	57
5	DMSO	1	B (20)	120	16	62
6	DMSO	0.5	B (40)	120	16	35
7	DMSO	1	B (40)	120	16	78
8	DMSO	0.05	<b>B</b> (40)	$120^{b}$	0.33	11
9	DMSO	1	B (40)	$120^{b}$	0.5	66
10	DMSO	1	<b>B</b> (40)	$120^{b}$	0.5	$75^c$
11	DMSO	2	<b>B</b> (40)	$120^{b}$	0.33	61
12	DMSO	2	B (40)	$120^{b}$	0.5	48
13	DMSO	2	B (40)	$120^{b}$	0.5	$60^c$
14	DMSO	1	<b>B</b> (80)	$120^{b}$	0.5	75
15	DMSO	1	<b>B</b> (60)	$85^b$	0.5	0
16	DMSO	2	B (40)	$100^{b}$	0.5	17
17	DMSO	1	<b>B</b> (40)	$150^{b}$	0.25	89 <sup>c</sup>
18	DMSO	10	B(40)	150 <sup>b</sup>	0.33	81 <sup><i>c</i>,<i>d</i></sup>

<sup>a</sup>In all experiments, 0.5 mmol of diacid was used.

<sup>b</sup>With microwave heating (temperature of IR sensor).

<sup>c</sup>The acid and catalyst were stirred for 5 min before adding AcOH and start microwave heating. <sup>d</sup>Using 5 mmol. reaction conditions used by Lu et al.<sup>[8d]</sup> for other compounds [10% mol Ag<sub>2</sub>CO<sub>3</sub> for carboxylic group, 0.05 mmol AcOH, dimethylsulfoxide (DMSO), 120 °C, 16 h] in our hands and using compound **1a** and conventional oil bath heating, gave a moderate yield of 54% (entry 2, Table 1), which is lower than using the Cu catalyst. An increment in the amount of Ag<sub>2</sub>CO<sub>3</sub> without adding more AcOH decreased the yield to 35% (entry 3, Table 1). This can be attributed to the AcOH neutralization with Ag<sub>2</sub>CO<sub>3</sub> excess. Kozlowski determined that in aromatic protodecarboxylation mediated by  $Pd(OCOCF_3)_2$ , the rate-limiting step is the protonation of Aryl-Pd intermediate, and thus 10-fold excess of the compound source of proton (CF<sub>3</sub>COOH) was required to complete the reaction.<sup>[6b,8d]</sup> After exploring different conditions (entries 3-6, Table 1), the compound 1a was protodecarboxylated in a yield similar to that with Cu catalyst and conventional heating, when 1 mmol of AcOH and 40% mol of Ag<sub>2</sub>CO<sub>3</sub> were used (entry 7, Table 1) after 16 h. These conditions are more convenient than the classical synthesis depicted in Scheme 1, because the reaction occurs at a temperature that is 30 °C lower, uses DMSO rather than quinoline as solvent, and uses a readily available and inexpensive proton source. Unfortunately a long reaction time was necessary for complete disappearance of the starting material using conventional heating. Therefore, to decrease the reaction time, microwave heating was explored.<sup>[9,10]</sup> Heating for 0.5h at 120 °C, with the optimized conditions found with conventional heating for the diprotodecarboxylation reaction, afforded an acceptable yield of 66% (entry 9, Table 1). However, a yield of 75% was reached when the experiment was repeated, after first stirring the carboxylic diacid and  $Ag_2CO_3$  in DMSO for 5 min, before the addition of AcOH and microwave heating (entry 10, Table 1). This pretreatment substantially favored the reactions (entries 12 and 13, Table 1). With a large excess of Ag catalyst, the yield is also good (entry 14, Table 1) and equivalent to that found with prestirring (entry 10, Table 1), demonstrating the advantage of this operation; nevertheless further experiments demonstrated that 40% per mol of compound (20% per mole of carboxylic group) was enough for carry out the reaction efficiently at low temperatures. A larger excess of the proton source compound was not beneficial for the reaction and the yield was lower (entries 11–13, Table 1). The use of temperatures lower than 120 °C provokes a drastic decrease of the yield (entries 15 and 16, Table 1). This temperature is in accordance with the increment in pression inside the reaction tube of reaction of the microwave reactor obseved when the temperature reaches 110 °C (Fig. SI-1), indicating that the diprotodecarboxylation reaction initiates at this temperature. Using the best conditions found for dicarboxylic compound **1a** at 120 °C (1 mmol AcOH + 40% mol Ag catalyst, corresponding to 20% per mole of carboxylic group + prestirring), the reaction was carried out at 150 °C during 15 min of microwave heating, leading to a greater yield very close to 90% (entry 17, Table 1). Finally, when the reaction was scaled to  $5 \text{ mmol using } 150 \,^{\circ}\text{C}$  (entry 18, Table 1) the product **2a** was obtained in a yield of 81%. In this reaction, the internal pressure in the vessel reached a constant maximum value of 12 bars after 20 min, which is a convinient and safe value for the reaction vessels used with the microwave system (max 30 bar). The utility and safety of the reaction conditions for larger-scale transformations was therefore demonstrated. The protodecarboxylation optimized conditions were tested with six additional analogs of 3,4-dialkoxythiophene-2,5dicarboxylic acids (1b-1g), and the results are shown in Table 2.

	Protodecarbox	Yield (%)			
Entry	Diacid	Product	Lit. Yield	120 °C 0.5 h	150 °C 0.25 h
1	$HO_2C$ $S$ $CO_2H$ 1a	H S H	54 <sup>[12]</sup>	75	89
2	HO <sub>2</sub> C SCO <sub>2</sub> H	H 2b	60 <sup>[4b]</sup>	78	81
3	HO <sub>2</sub> C S CO <sub>2</sub> H	CH <sub>3</sub> O H S 2c	64 <sup>[4b]</sup>	83	86
4	$HO_2C$ $S$ $CO_2H$ $Id$	Ph H S 2d	54 <sup>[4b]</sup>	53	76
5	HO <sub>2</sub> C S CO <sub>2</sub> H	H 2e	45 <sup>[4b]</sup>	78	80
6	$HO_2C$ $S$ $CO_2H$ 1f	H S H S H	_	44	56

 Table 2. Diprotodecarboxylation of 3,4-dialkoxythiophene-2,5-dicarboxylic acids, 1a-1g

(Continued)

	Protodecarb	Yield (%)			
Entry	Diacid	Product	Lit. Yield	120°C 0.5 h	150°C 0.25 h
7	Ph O HO <sub>2</sub> C S CO <sub>2</sub> H	Ph O O H	_	22 <sup>b</sup>	37 <sup>b</sup>
	- <u>3</u> - 1g	2g			

Table 2. Continued

<sup>a</sup>Using 0.5 mmol of compound **1**, 1 mmol of AcOH, 40% mol Ag<sub>2</sub>CO<sub>3</sub>, prestirring of diacid and catalyst, and microwave heating.

<sup>b</sup>Main product.

The 3,4-dialkoxythiophenes 2a-2e had been prepared by means of the classic method with the Cu catalyst-quinoline system,<sup>[4b,11]</sup> and for comparison the reported yields are depicted also in Table 2. As occurred with compound **1a**, the corresponding 3,4-dialkoxythiophenes were obtained in greater yields and shorter heating times (0.5 h) using lower temperature  $(120 \,^{\circ}\text{C})$  than the previously reported with Cu catalyst and without the harmful solvent quinoline (entries 2-5, Table 2). Increasing temperature to 150 °C resulted in a slight increase in yield (3–23% depending upon the product) with a time of reaction of only 15 min. Nevertheless, in the case of sensitive compounds, limiting the microwave heating to  $120 \,^{\circ}$ C is enough to obtain the target compounds in good yields. O-Alkyl substituted derivatives such as 2f are prepared throughout trans-etherification of 3,4-dimethoxy-thiophene,<sup>[2g,12a]</sup> a compound that is relatively unstable. The present method overcomes this difficulty. The double protodecarboxylation of 1g was not possible to achieve, because of a fast intramolecular reaction between the acetal and one carboxylic group of the diacid that produces, mainly lactone 2g and benzaldehyde. The identity of this compound was confirmed by NMR (see Suporting Information) and x-ray crystallography (Fig. I). The two enantiomers are present in the crystal of compound 2g as a racemate and it shows planarity among the thiophene ring, the carboxylic group, the hydroxyl group, and the ethereal oxygen. Carbon 6 is 0.635 A out from this plane, so the conformation



Figure 1. Crystal structure of 2g. Ellipsoids are drawn at the 50% probability level for non-H atoms.



Scheme 2. Proposed mechanism reaction to achieve 2g.

of the six-membered ring is half-chair, the same conformation to reported in compounds with similar six-membered ring fused to benzene.<sup>[13]</sup>

To determine if the intramolecular reaction of 1g occurs before or after the protodecarboxylation reaction, it was followed by <sup>1</sup>H NMR, heating the NMR tube containing all the required reactants, but without the catalyst (Ag<sub>2</sub>CO<sub>3</sub>) (Fig. SI-2). The experiment showed that spontaneous decarboxylation was possible when temperature reaches 55 °C, resulting in products 2g and benzaldehyde. The same products were detected if the protodecarboxylation reaction is attempted without AcOH (to minimize the acetal opening), showing that the reaction is not catalyzed by this acid. A mechanism to explain the transformation of 1g to 2g is proposed in Scheme 2, where an intramolecular hydrogen bonding between the acetal unit of 1g and the acidic proton of one of the carboxylic acids promotes the 1,3-dioxalane system opening. At the end of this rearrangement only one carboxylic acid is available to react in the protodecarboxylation reaction.

# CONCLUSION

In conclusion, Larrosa et al.'s protodecarboxylation procedure was modified and adapted to carry out efficiently and rapidly diprotodecarboxylation of 3,4dialkoxythiophen-2,5-dicarboxylic acids using 40% mol  $Ag_2CO_3$  (20% per mole of carboxylic group), 2 equivalents of AcOH, and prestirring of the diacid and the catalyst prior to microwave heating in the temperature range 120–150 °C. This methodology was applied to seven different substrates showing greater yields than the classical Cu catalyst-quinoline protocol, eliminating the harmful quinoline and saving energy because of the short time required in the reaction.

#### **EXPERIMENTAL**

All microwave reactions were carried out in closed vials using microwave reactor Synthos 3000 from Anton Paar. Anhydrous DMSO, glacial AcOH, copper

chromite, AgNO<sub>3</sub>, and anhydrous Na<sub>2</sub>CO<sub>3</sub> were purchased from Sigma Aldrich, and Merck Mallinckrodt, and used without further purification. <sup>1</sup>H NMR spectra were recorded at 300 MHz and are referenced to the residual solvent peak at 7.26 ppm (CDCl<sub>3</sub>), 2.09 ppm (acetone-d<sub>6</sub>), and 2.50 ppm (DMSO-d<sub>6</sub>). <sup>13</sup>C NMR spectra were recorded at 75 MHz and are referenced to the solvent peak at 77.0 ppm (CDCl<sub>3</sub>), 29.9 and 206.7 ppm (acetone-d<sub>6</sub>), and 39.5 ppm (DMSO-d<sub>6</sub>).

# General Procedure for Protodecarboxylation of 3,4-Dialcoxythiophene-2,5-dicarboxylic Acids

The mixture of 3,4-dialcoxythiophene-2,5-dicarboxylic acid (0.5 mmol) and  $Ag_2CO_3$  (0.20 mmol, 55.15 mg) in DMSO (1.0 mL) was magnetically stirred. After 5 min, AcOH (1 mmol, 56 µl) was added, the microwave tube was closed, and the mixture was heated using the microwave reactor. The reaction was carried out for 30 min for the experiments conducted at 120 °C and for 20 min when they were carried out at 150 °C. After microwave heating, the reaction was cooled to room temperature and quenched with 2 M HCl (2 mL), the mixture was filtered, and the aqueous phase was extracted with EtOAc (5 × 5 mL). The combined organic layers were washed with brine (2 × 25 mL) and dried (Na<sub>2</sub>SO<sub>4</sub>). Concentration under reduced pressure gave a crude product, which was purified by flash chromatography in silica gel using n-hexane–CH<sub>2</sub>Cl<sub>2</sub> 80:20 as eluent.

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