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### Ritter Reactions between Alcohols and Acetonitrile Mediated by the Conducting Polymer Poly-(3,4-ethylenedioxy Thiophene) (PEDOT)

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## RITTER REACTIONS BETWEEN ALCOHOLS AND ACETONITRILE MEDIATED BY THE CONDUCTING POLYMER POLY-(3,4-ETHYLENEDIOXY THIOPHENE) (PEDOT)

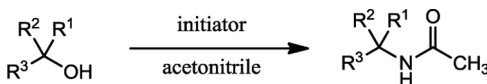
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### GRAPHICAL ABSTRACT



**Abstract** Herein, we report new reactivity of the conducting polymer, poly-(3,4-ethylenedioxy thiophene) (PEDOT), where PEDOT mediates a Ritter reaction between alcohols and acetonitrile. The yields were variable and in most cases competitive with results obtained using sulfuric acid. Attempts at a stoichiometric reaction between benzonitrile and diphenylmethanol are also reported herein. Finally, described here are preliminary mechanistic studies that suggest PEDOT is behaving as an alcohol-selective or specific Lewis acid.

Supplementary materials are available for this article. Go to the publisher's online edition of Synthetic Communications<sup>®</sup> for full experimental and spectral details.

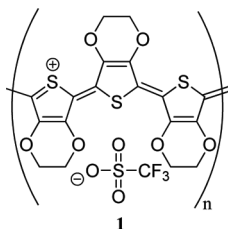
**Keywords** Alcohol; amide; conducting polymer; PEDOT; Ritter

## INTRODUCTION

Recently, the conducting polymer poly-(3,4-ethylenedioxy-thiophene) (PEDOT) (**1**, Fig. 1)<sup>[1]</sup> was reported to initiate formation of homoethers from alcohols with small amounts of oxidation to the corresponding ketone or aldehyde<sup>[2]</sup> Friedel–Crafts alkylations of benzene and toluene with alcohols<sup>[3]</sup> and cyclodehydrations of acyclic sugars<sup>[4]</sup>—suggesting acid-like behavior. Other conjugated polymers have also been used to mediate chemical reactions, such as protonated polyaniline salts with counteranions such as SO<sub>4</sub><sup>2-</sup> or NO<sub>3</sub><sup>-</sup> for the tetrahydropyranylation of alcohols;<sup>[5]</sup> protonated polyaniline salts with counteranions such as SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, or

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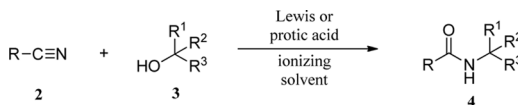
**Figure 1.** Chemical structure of PEDOT employed in this study. The polymer is a repeating trimer unit containing a single positive charge counterbalanced by one triflate counterion.

$\text{NO}_3^-$  for transesterification reactions;<sup>[6]</sup> protonated polyaniline salts with  $\text{SO}_4^{2-}$ , a counteranion for acetal formation and deprotection;<sup>[7]</sup> polypyrrole with Pd(0) or Pd(II) to hydrogenate nitrobenzene to aniline;<sup>[8]</sup> and polypyrrole-based heteropoly acid catalysts for eliminations and oxidations on alcohols.<sup>[9]</sup> These and other reactions employing modified conjugated polymers were recently reviewed.<sup>[10]</sup> In each of the aforementioned cases, acids such as  $\text{H}_2\text{SO}_4$  or other additives are added to the polymer or incorporated into the polymer backbone. In contrast, for the reactions using PEDOT,<sup>[2–4]</sup> including those described herein, no such acids are added during or after polymerization, suggesting that these reactions are somehow mediated by PEDOT.

The use of PEDOT to initiate reactions is advantageous as a heterogeneous catalyst, which permits ease of purification, workup, and potential recycling. Because PEDOT does not have functionality bound to it (i.e., amines or sulfonic acid) the mode of reaction should prove to be different, and those differences should result in chemoselectivity to the alcohol functionality and synthetically viable reactivity differences among 1°, 2°, and 3° alcohols. Additionally, an improved fundamental understanding of PEDOT's ability to catalyze reactions such as the Ritter reaction may result in the development of novel polymer catalysts with lower preparation cost and perhaps improved selectivity.

Because PEDOT and other polymeric reagents are used as heterogeneous mixtures, we turned our attention to exploring the utility of PEDOT in mediating chemical transformations of alcohols traditionally initiated by Lewis and/or protic acids. Subsequently, we discovered that when alcohols are treated with PEDOT in acetonitrile at reflux, a Ritter reaction occurs between the alcohol and acetonitrile to furnish the corresponding acetamide.

The Ritter reaction (Scheme 1)<sup>[11,12]</sup> generates amides/amide-protected amines from a carbocation, a nitrile, and lactams in cases where reaction occurs intramolecularly. The currently accepted mechanism involves nucleophilic attack of the cation by the nitrile with subsequent nucleophilic attack of the intermediate nitrilium ion by the conjugate base of the mediating acid to furnish an imidate.<sup>[13]</sup> The resulting imidate is then hydrolyzed to give the amide product. Substrates for the Ritter reaction have included alcohols, halides, and alkenes, with the concurrent treatment of the substrate with an appropriate Lewis or protic acid, typically employing a strongly ionizing solvent such as acetic acid. The use of catalysts (Lewis and protic acids) to mediate Ritter reactions was recently reviewed.<sup>[14]</sup> Recently, it has been



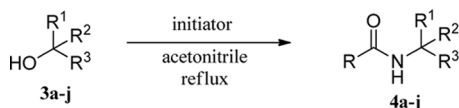
Scheme 1. General Ritter reaction.

shown that silica<sup>[15,16]</sup> or polymer-supported<sup>[17]</sup> acids as well as ionic liquids<sup>[18]</sup> are effective at mediating these reactions as well.

## DISCUSSION











To simultaneously explore the scope of our PEDOT protocol and compare the results to more traditional conditions, we separately treated the alcohols in this study with Amberlyst-15, H<sub>2</sub>SO<sub>4</sub>, and PEDOT in acetonitrile at reflux as described in Scheme 2 and Table 1. The Amberlyst and sulfuric acid-mediated Ritter reactions generated amides **4** in good yields in cases where the carbocation intermediate was stabilized (Table 1, entries 1–4, 6, and 7). In all cases studied, sulfuric acid-mediated reactions had faster rates of conversion than the Amberlyst-mediated reactions. The substrate cyclohexanol (**3j**) was converted in poor yields to amide **4j**, with the major by-product being cyclohexene, as observed by gas chromatography–mass spectrometry (GCMS). It is reasonable to conclude that in cases of alcohols that have β-hydrogens available for elimination the appropriate alkene is the major by-product, although not isolated in the current study because of their low boiling points (Table 1, entries 5, 6, 8, and 9). In alcohol substrates where elimination is not possible, the yields increase significantly. Additionally, with primary alcohols **3a**, **3h**, and **3i** observed by-products were the acylated alcohols, benzyl acetate, and *iso*-butyl acetate and butyl acetate, respectively, in reactions with H<sub>2</sub>SO<sub>4</sub>.

The PEDOT-mediated Ritter reactions provide greater yields of amides **4** in each case where the amide was observed with PEDOT (Table 1, entries 2, 3, and 7). Interestingly, the reactivity of PEDOT seems orthogonal to the traditional Ritter conditions for the tertiary alcohols. For instance, triphenylmethanol (**3d**) provides trace quantities of amide **4d** found by GCMS, along with the reduction product, triphenyl methane, and small amounts of what appears to be a product consistent with spectral data for 9-phenylfluorene. Mediation by Amberlyst and H<sub>2</sub>SO<sub>4</sub> provided yields of 96 and 87% of the desired amide **4d**, respectively. These differences suggest that the alcohol -OH may need to coordinate with the PEDOT in order to react. This accounts for the reduced activity with PEDOT because the traditional acids liberate an electrophilic H<sup>+</sup>, whereas interactions with PEDOT must overcome a steric approach to the positively charged polymer backbone to react. We are particularly excited about the 1-adamantanol case (Table 1, entry 7), which furnished



Scheme 2. General Ritter reaction performed.

**Table 1.** Summary of results with H<sub>2</sub>SO<sub>4</sub>, Amberlyst, and PEDOT-mediated reactions of alcohols with acetonitrile

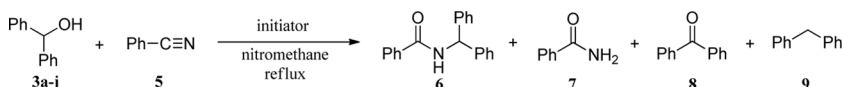
Entry	Alcohol <b>3</b>	Initiator	Isolated yield of <b>4</b> (%)
1	 <b>3a</b>	Amberlyst	12
		H <sub>2</sub> SO <sub>4</sub>	63
		PEDOT	<1
2	 <b>3b</b>	Amberlyst	40
		H <sub>2</sub> SO <sub>4</sub>	48
		PEDOT	70
3	 <b>3c</b>	Amberlyst	70
		H <sub>2</sub> SO <sub>4</sub>	85
		PEDOT	91
4	 <b>3d</b>	Amberlyst	96
		H <sub>2</sub> SO <sub>4</sub>	87
		PEDOT	<1
5	 <b>3e</b>	Amberlyst	<1
		H <sub>2</sub> SO <sub>4</sub>	14
		PEDOT	Not detected
6	 <b>3f</b>	Amberlyst	44
		H <sub>2</sub> SO <sub>4</sub>	66
		PEDOT	Not detected
7	 <b>3g</b>	Amberlyst	48
		H <sub>2</sub> SO <sub>4</sub>	53
		PEDOT	83
8	 <b>3h</b>	Amberlyst	Not detected
		H <sub>2</sub> SO <sub>4</sub>	Not detected
		PEDOT	Not detected
9	 <b>3i</b>	Amberlyst	<1
		H <sub>2</sub> SO <sub>4</sub>	<1
		PEDOT	Not detected
10	 <b>3j</b>	Amberlyst	<1
		H <sub>2</sub> SO <sub>4</sub>	18
		PEDOT	Not detected

amide **4g** in very good yield (>80%) with PEDOT and more modest 48 and 53% yields with Amberlyst and H<sub>2</sub>SO<sub>4</sub>, respectively. We found that this reaction proceeded far more slowly than all of the others with PEDOT, taking ~32 h to reach a point of no further consumption of alcohol by GCMS with an isolated yield of 83%. This longer reaction time is consistent with the premise that sterics may hinder the approach of the alcohol to the polymer, further supporting this mode of reactivity over one that involves H<sup>+</sup>. Secondary alcohols **3e** and **3j** suffered from poor reactivity with Amberlyst and H<sub>2</sub>SO<sub>4</sub> and no observed reactivity with PEDOT (Table 1, entries

5 and 10). Of note is the poor reactivity of benzyl alcohol (**3a**) compared to 1-naphthalene methanol (**3b**) with PEDOT. In the case of 1-naphthalene methanol (Table 1, entry 2) nearly all of the alcohol was consumed in the reaction with PEDOT after ~4 h, furnishing, after purification, the desired amide in 70% isolated yield. This observed reactivity of PEDOT is consistent with previous reports where Friedel–Crafts reactions with 1-naphthalene methanol proceeded better than benzyl alcohol in benzene at reflux.<sup>[3]</sup> It is possible that the greater conversion observed for the naphthyl system compared with the benzyl system, when using PEDOT, may be due to the naphthyl system interacting more favorably with the PEDOT than benzyl alcohol or trityl alcohol. The case of diphenylmethanol (Table 1, entry 3) was the most efficient PEDOT-mediated reaction. After only 3 h, all of the starting material was completely consumed by GCMS, giving rise to a single product that corresponded to amide **4c** in 91% isolated yield after purification.

We next investigated if this reaction could be performed with more complex nitriles in a nonnitrile solvent (Scheme 3). After a survey of solvents, we identified nitromethane as a suitable solvent for this purpose. Again, as with acetonitrile, we compared the results obtained using PEDOT with a more traditional initiator, sulfuric acid (Table 2). Although the PEDOT conditions are unoptimized, we demonstrate here that PEDOT can be used as a mediator in a Ritter reaction between alcohols and nitriles in nonnitrile solvents. We were surprised to find the oxidation product, **8**, become the major product in the 2.0 eq. case (Table 2, entry 2). Using 5 equivalents of benzonitrile, the major product shifts to the desired amide **6**, though the yield (22%) is far inferior to that from H<sub>2</sub>SO<sub>4</sub> (88%). It is unclear at this time whether the increased equivalence of nitrile in this case (Table 2, entry 4 vs 2) is somehow chemically responsible for the decrease in yield of **8**. Previous studies showed oxidation to be a minor pathway.<sup>[2]</sup> The source of the oxidation by-products of PEDOT reactions with alcohols remains unknown, but is interesting that polypyrrole-based heteropoly acid catalysts have been used for the oxidation of alcohols.<sup>[9]</sup> It is also noteworthy that the reaction with PEDOT yielded significantly less hydrolysis product of the nitrile to the primary amide, compared to H<sub>2</sub>SO<sub>4</sub>, as would be expected, which further emphasizes the chemoselectivity of PEDOT.

In an attempt to demonstrate the selectivity of PEDOT for alcohols and investigate the mechanism, we, in separate reactions, also attempted a reaction between styrene and benzyl chloride with PEDOT in refluxing acetonitrile. In both cases, after 2 h, no reaction was observed by GCMS. Based on our experience from monitoring our reactions, if the reaction were going to furnish product, 2 h is enough time to generate detectable product. Furthermore, PEDOT appears to preferentially react with alcohols in the presence of alkenes, as seen when we attempted the tetrahydropyranylation of 1-naphthalene methanol using PEDOT in benzene along with 3,4-dihydro-2H pyran, under reflux. The major products of this chemical reaction were found by GC/MS to be di-1-naphthylmethylether and the Friedel–Crafts



**Scheme 3.** Stoichiometric Ritter reaction performed.

**Table 2.** Stoichiometric Ritter reactions between diphenyl methanol and benzonitrile mediated by PEDOT and H<sub>2</sub>SO<sub>4</sub>

Entry	Equivalence of <b>5</b>	Initiator	Isolated yield (% based on <b>3c</b> )				Isolated yield (% based on <b>5</b> )	
			<b>3c</b>	<b>6</b>	<b>8</b>	<b>9</b>	<b>5</b>	<b>7</b>
1	2	H <sub>2</sub> SO <sub>4</sub>	ND	73	3 <sup>a</sup>	<1 <sup>a</sup>	ND	46
2	2	PEDOT	ND	8	21 <sup>b</sup>	8	20 <sup>b</sup>	12
3	5	H <sub>2</sub> SO <sub>4</sub>	ND	88	ND	ND	18	38
4	5	PEDOT	ND	22	12 <sup>b</sup>	6	5 <sup>b</sup>	6

<sup>a</sup>**8** and **9** were not separated during purification. Ratios as determined by <sup>1</sup>H NMR integration are 4:1 of **8/9** (% calculated).

<sup>b</sup>**5** and **8** were obtained as an inseparable mixture. Ratios as determined by <sup>1</sup>H NMR integration are 2:1 of **5/8** for entries 2 and 4 (% calculated).

Note. ND, not detected.

alkylation product between the putative 1-naphthyl cation and benzene. By contrast, when using Amberlite IRE-50(H) as the initiator, the major product was the desired tetrahydropyranyl ether according to GCMS, similar to polyaniline salts loaded with H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>.<sup>[5]</sup> Thus, PEDOT appeared to prefer to react with the naphthalene methanol, rather than the 3,4-dihydro-2H pyran, whereas the Amberlite IRE-50(H) preferred to react with the pyran. These results demonstrate that PEDOT reacts at least selectively and perhaps specifically with alcohols and not halides or alkenes. In another reaction, we reacted a 1:1 mixture of cyclohexanol and 1-naphthalene methanol in acetonitrile. In this case, only *N*-1-naphthalenemethyl acetamide and unreacted cyclohexanol along with very small amounts of unreacted 1-naphthalene-methanol were observed. This result is important because it insinuates a selectivity of PEDOT for aromatic over aliphatic alcohols under these reaction conditions, which may be taken advantage of in total synthesis by eliminating the need for protection and deprotection steps. We are currently exploring the selectivity to include developing more complex systems, including diols, to further evaluate this potential selectivity.

## EXPERIMENTAL

### Example of Method A: Ritter Reactions Mediated by Sulfuric Acid with Acetonitrile as Solvent

Sulfuric acid (0.80 mL, 15.0 mmol) was added dropwise to a parallel reactor vial containing diphenylmethanol (1.00 g, 5.43 mmol) and acetonitrile (20.0 mL, 383 mmol). The reaction was stirred at reflux until the alcohol was consumed (monitored by GCMS) and then quenched with sodium bicarbonate (saturated, 25 mL). The resulting mixture was extracted with ethyl acetate (3 × 15 mL) and the combined organics were washed with brine (saturated, 18 mL), dried over magnesium sulfate, filtered, and concentrated in vacuo to give the crude reaction products, which were purified by radial chromatography to give *N*-benzhydrylacetamide (**4c**) as a white solid (1.02 g, 85%).



**Example of Method B: Ritter Reactions Mediated by Amberlyst-15 with Acetonitrile as Solvent**

Amberlyst-15 hydrogen form (1.81 g) was added to a parallel reactor vial containing diphenylmethanol (1.00 g, 5.43 mmol) and acetonitrile (20.0 mL). The reaction was stirred at reflux for 72 h and then filtered to remove Amberlyst. The filtrate was diluted with 25 mL water and quenched with sodium bicarbonate (saturated, 2 mL). The aqueous was then extracted with ethyl acetate ( $3 \times 15$  mL) and the combined organics were washed with brine (saturated, 18 mL), dried over magnesium sulfate, filtered, and concentrated in vacuo to give *N*-benzhydrylaceta-mide (**4c**) as a white solid (0.85 g, 70%).

**General Method C: Ritter Reactions Mediated by PEDOT with Acetonitrile as Solvent**

PEDOT (200 mg) was added to a round-bottomed flask containing acetonitrile (25 mL) and the alcohol (1.00 mmol). The reaction was stirred at reflux until the alcohol was consumed (monitored by GCMS), filtered, and concentrated in vacuo to give the crude reaction products, which were purified by flash chromatography when warranted.

**General Method D: Stoichiometric Ritter Reactions Mediated by Sulfuric Acid with Nitromethane as Solvent**

Sulfuric acid (0.60 mL, 10.9 mmol) was added to a parallel reactor vial containing diphenylmethanol (1.00 g, 5.43 mmol), nitromethane (20 mL), and benzonitrile (variable). The reaction was stirred at 86 °C for 3 h until the limiting reagent was consumed (monitored by GCMS). Upon cooling to rt, the reaction was quenched with sodium bicarbonate (saturated, 20 mL). The resulting mixture was extracted with ethyl acetate ( $3 \times 20$  mL) and the combined organics were washed with brine (50%, 20 mL), dried over magnesium sulfate, filtered, and concentrated in vacuo to give the crude reaction products. The off-white solid was purified by flash chromatography (2% ethyl acetate/hexanes to 100% ethyl acetate) to give the products.

**General Method E: Stoichiometric Ritter Reactions Mediated by PEDOT with Nitromethane as Solvent**

PEDOT (150 mg) was added to a parallel reactor vial containing diphenylmethanol (138 mg, 0.75 mmol), nitromethane (8 mL), and benzonitrile (variable). The reaction was stirred at reflux for 3 h until the limiting reagent was consumed (monitored by GCMS). Upon cooling to rt, the reaction was filtered and washed with dichloromethane to recover PEDOT, and then the filtrate was filtered and washed with dichloromethane through Celite. The filtrate was concentrated in vacuo to give the crude reaction products. The residue was purified by flash chromatography (2% ethyl acetate/hexanes to 100% ethyl acetate) to give the products.

**N-Benzhydrylacetamide (4c)**

$^1\text{H}$ NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.36–7.20 (m, 10H), 6.32 (br d,  $J = 8.1$  Hz, 1H), 6.23 (d,  $J = 8.1$  Hz, 1H), 2.01 (s, 3H);  $^{13}\text{C}$ NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  169.4, 141.6, 128.9, 127.4, 127.5, 57.0, 23.2; MS (EI):  $m/z = 225$  ( $\text{M}^+$ ); cf. spectrum reported.<sup>[19]</sup>

**SUPPORTING INFORMATION**

Full experimental details with  $^1\text{H}$  and  $^{13}\text{C}$  NMR reports can be found via the Supplementary Content section of this article's Web page.

**CONCLUSIONS AND FUTURE WORK**

We have shown that the conducting polymer PEDOT mediates a Ritter reaction between activated alcohols and nitriles. Although the mechanism by which PEDOT mediates this reaction is still under investigation, the work herein and ongoing suggests that it is behaving as a chemoselective Lewis acid that prefers to react with alcohols. Moreover, with the unreactivity of styrene in mind, coupled with the result of the experiment with the tetrahydropyranylation, it appears that the reaction is not initiated by putative small quantities of triflic acid embedded in or adsorbed by the polymer that could have been produced during the polymerization. For the same reason, we do not think that we are generating triflic acid during the reaction and therefore argue that the PEDOT is behaving as a Lewis acid. This hypothesis is further supported by the sluggish reactions with 1-adamantanol and virtual lack of reactivity with triphenyl methanol, which is likely a steric effect. If triflic acid were somehow present,  $\text{H}^+$  would be the reactive unit and there would be little to no influence of steric hindrance around the alcohol OH.

Given the number of natural and pharmaceutical products that contain an amide or amine moiety, further exploration of the PEDOT-mediated Ritter reactions is warranted. Using a survey of nitriles in nonnitrile solvents we hope to generate a method that converts an activated alcohol chemoselectively in the presence of other moieties such as unprotected alcohols, alkenes, and halides to amides/amide-protected amines. Additionally, further exploration of PEDOT's ability to mediate other reactions employing alcohol substrates is under way. We also have begun studies that examine the polymer before and after the reaction. We anticipate that this will lead to the generation of lower cost reactive conducting polymers.

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