Organic Chemistry Research

Minireview

Organic Chemistry Research
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Cite this: *Org. Chem. Res.* **2022**, *Vol. 8,* 70-73.
DOI: 10.22036/org.chem.2024.437057.1318

Electrochemical PINOylation Reactions of Organic Compounds

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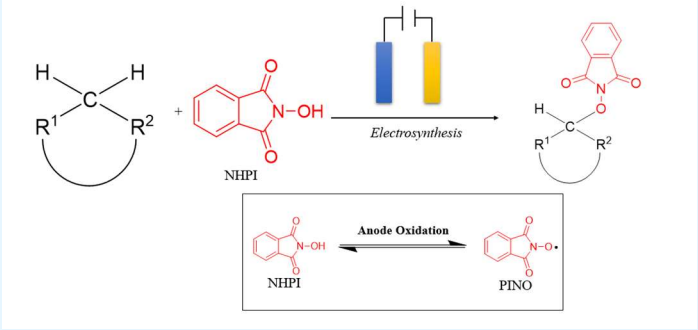
Received: January 21, 2024; Accepted: January 24, 2024

Minireviews-Spotlight: This feature focuses on a reagent and subject chosen by a postgraduate, highlighting the hot topic subjects or uses and preparation of the reagent in current research.

Abstract: The synthesis of compounds by electrochemical method is one of the powerful tools in the preparation of different chemical structures, which has made great progress in recent years. Preparation of stable intermediates is very important and electrochemical syntheses have been able to work very successfully in this case, one of them can be called PINOylation of various chemical compounds by electrochemical method. PINOylation is a very important process and can be synthesized stable intermediates and more complex structures and various compounds. Although there are few reports on PINOylation of organic compounds by electrochemical method. but these few reports, can be called as the beginning of the synthesis period by the electrochemical PINOylation method.



Keywords: *N*-hydroxyphthalimide (NHPI), Phthalimide *N*-Oxyl (PINO), PINOylation, Electrosynthesis, Electrochemical synthesis.

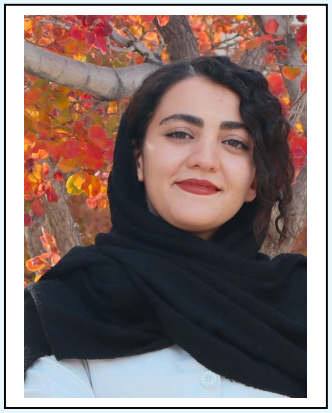
1. Introduction

In the last two decades, the synthesis of various compounds by electrochemical method has attracted much attention of scientists. By using this synthesis method, they were able to prepare different molecules that were very difficult to prepare in a non-electrosynthesis method. In this method, they mainly use solvents, solvents, electrodes and electrolytes for synthesis.[1-4]

Recently, more studies are conducted on the electrochemical properties of N-hydroxyphthalimide (NHPI) and it is used in various electrochemical reactions. Currently, NHPI is known as one of the important electrochemical catalysts in chemical, pharmaceutical and industrial research.[5-14] NHPI is an organic compound with electrochemically active positions. NHPI was first developed by the German chemist Hans von Euler-Chelpin in 1928, but was specifically applied to electrochemical studies in the 1960s. In these years, several chemists started to study the electrochemical reactions of NHPI.[15,16] In 1983, Masui and Ozaki demonstrated the ability to obtain Phthalimide N-Oxyl (PINO) from NHPI under electrochemical conditions.[17] Electrolysis experiments showed that unlike hydroxamic acids that undergo $2e^-$ electrochemical oxidation, NHPI undergoes $1e^-$ oxidation to form PINO.[18] showed this reaction in acetonitrile with a redox potential of 1.44V vs. SCE and called this process quasi-reversible. Adding one or two equivalents of pyridine to the reaction mixture changes the potential of NHPI to 0.85 and 0.78 V vs. SCE in acetonitrile solvent, respectively.[19]

NHPI is usually used as an agent to convert alcohols into carbonyls in electrochemical environments, which is done in this way. When NHPI becomes PINO, it causes the substance to lose an electron and then the reaction proceeds through the radical path and converts the alcoholic substance into a carbonyl substance, recently, there have been reports of intermediate control of PINO and on the main compound, which has also been isolated. It should be noted that although the use of NHPI as a catalyst in electrosynthesis processes is very common,[20] But the preparation of intermediates with PINO has much more values, stable intermediates with PINO can be used in the preparation of complex structures and other different compounds Electrochemical synthesis processes are among those that have recently been able to stabilize PINO intermediates, and few reports are available in this research field and researchers and research groups can work more on this to get new and useful data.

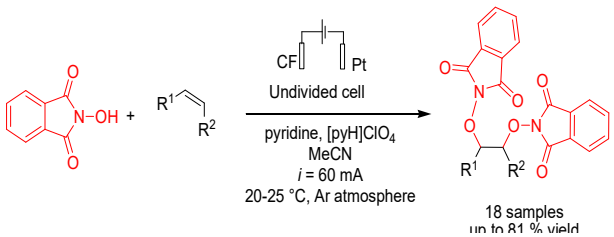
Milad Behroozi was born in 1997 in Iran. He studied Chemistry at University of Maragheh, Maragheh, Iran, where he obtained his bachelor's degree in September 2019. Then the next year, he joined Professor Babak Kaboudin's Electrochemical Synthesis group at the Institute for Advanced Studies in Basic Sciences (IASBS) in Organic chemistry filed, where he completed his master's thesis in September 2023. His research interests include electrosynthesis, organophosphorus compounds, heterocycle synthesis, phytochemistry and the catalytic application of nanomaterials.



Sepideh Sadighi was born in 1998 in Iran. She obtained her bachelor's degree at University of Maragheh, Maragheh,- Iran, in 2020. In the same year, she went to Institute for Advanced Studies in Basic Sciences (IASBS) and joined Professor Babak Kaboudin's Electrochemical synthesis research group and earned her master's degree in September 2023. Currently, she's research interest is organic synthesis and electrochemical synthesis.

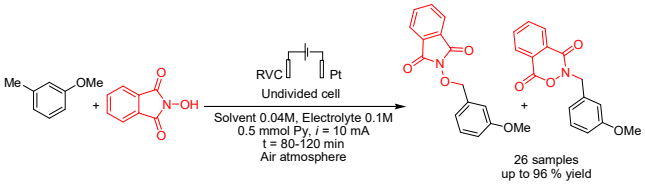
2. Electrochemical PINOylation reactions

NHPI is usually reported as an intermediate in electrochemical reactions, and less attention has been paid to the fact that it can react with the starting material in question and produce the product. But recently, there have been reports of reactions in which NHPI has created a link with another substance, and we will examine some of them below. Terent'ev's research group and colleagues reported in an article that they were able to stabilize the PINO compound on C(sp^2) in 2021, while in this report they mentioned the use of pyridine as a base pyridine is very poisonous and dangerous, graphite and platinum electrodes have been used as anode and cathode in this research (Scheme 1).[21]



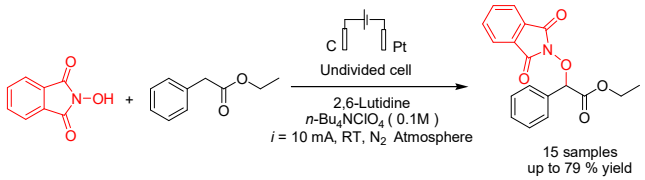
Scheme 1. Anodically Induced dioxygenation of Vinyl Arenes with N-Hydroxyphthalimide

Later, another report was reported by Stahl and co-workers in 2022, but this group aimed to stabilize PINO to create an intermediate for the photochemical reaction; This group succeeded in stabilizing PINO on C(sp^3) while the carbon position was supported by an electron-rich group; But in this reaction, like the previous reaction, pyridine was used as a base and RVC|Pt electrodes were used as anode and cathode (Scheme 2).[22]



Scheme 2. Electrochemical PINOylation of Methylarenes

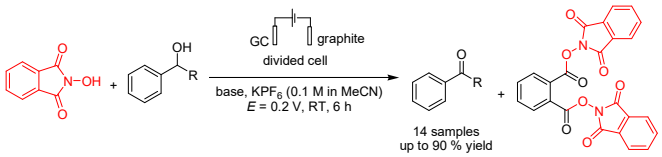
Hu *et al.*, in a report, investigated the electrocatalytic properties of N-hydroxyphthalimide (NHPI) in the presence of phenylacetate derivatives. In this study, they were able to convert NHPI to its radical form, Phthalimido-N-oxyl (PINO) and make it stable on the molecular structure; They were able to obtain different variations of this product and observed the yield of the product up to 79% (Scheme 3).[23]



Scheme 3. Phenylacetate derivatives and NHPI electrochemical reaction

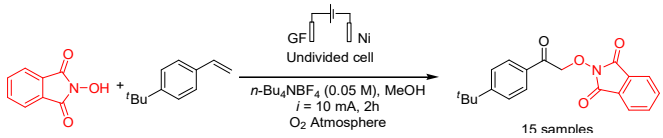
Yang's research group performed an electrochemical reaction with the aim of converting alcohol to the corresponding ketone, and in addition to the product in question, they identified a different product resulting from the reaction of PINO with NHPI in the environment. In this reaction, like other reactions from pyridine was used as a base in the environment, pyridine has played an essential role in the mechanisms of this group of reactions in the conversion of

NHPI to PINO. In this reaction, glassy-carbon (GC) and graphite electrodes were used as anode and cathode, and the reaction was carried out at constant potential and in the presence of pyridine base. The yield of the desired ketone product was obtained with 90% and the side product obtained from the reaction of PINO with NHPI was also obtained (Scheme 4).[24]



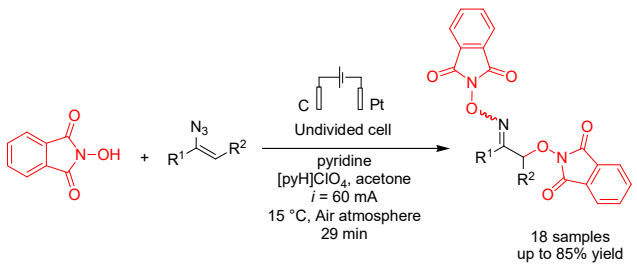
Scheme 4. Alcohol and NHPI electrochemical reaction

Styrenes have various synthetic, pharmaceutical and industrial applications. Examining the electrosynthesis processes of these compounds is very important. Zhang *et al*., in a report on the use of styrenes in the presence of NHPI, they were able to stabilize the structure of PINO on styrenes, which is a valuable intermediate for the synthesis of various molecules (Scheme 5).[25]



Scheme 5. Styrenes and NHPI electrochemical reactions

Terent'ev and co-workers also reported a report on the stabilization of PINO by α-Azido Styrenes; In this process, unlike the previous reaction, it takes advantage of the existence of the nitrogen group and creates a bond between oxygen and nitrogen by electrochemical method, which is accompanied by the release of nitrogen gas; In this process, pyridine has been used as an effective agent, because the



Scheme 6. α-Azido Styrenes and NHPI electrochemical reaction

efficiency of the process is greatly reduced by removing it, this group has mentioned in their reports that the final product is in the spatial isomer state and they have used the electrosynthesis process using C|Pt electrodes as anode and cathode.[26]

3. Conclusion

In recent reactions, NHPI has shown that in addition to catalytic activity, it can act as a reactant and produce stable intermediates, which are very important from the point of view of application, because more complex structures can be obtained with this method.

The electrosynthesis method of these compounds has been very successful and has been able to create intermediates with PINO and can be used as a powerful tool in the laboratory for the synthesis of these compounds.

Declaration of Interests

The author declare that she/he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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