

Electron Flow: A Versatile Tool to Inspire Organic Synthesis



KID: 20230409

In response to the imperative of achieving sustainable development goals and addressing societal demands for environmentally friendly chemistry, there has been a keen focus on the development of green chemical strategies and technologies that utilize clean energy sources. As a result, numerous methodologies have emerged, and electro-organic synthesis is becoming one of the increasingly versatile tools in organic synthesis due to its potential to provide sustainable and environmentally friendly alternatives to traditional chemical synthetic routes.[1–4] This electrochemical method has gained significant interest from worldwide synthetic chemists and industry and opened strategic pathways in organic synthesis toward synthesizing pharmaceutically and biologically essential products. [5,6] A notable surge in the development of electrochemical organic synthesis has been witnessed, particularly in the last decade. Contrasting with early approaches based on inherent reactivity, researchers have recently integrated creative conceptions of organic syntheses into these eco-friendly approaches. Electrochemical organic synthesis is a branch of organic chemistry that utilizes electrochemical methods to facilitate and control chemical reactions. It is the process of synthesizing organic compounds merely by using electricity. Utilizing the power of electricity provides unique advantages, such as improved selectivity, milder reaction conditions, and reduced environmental impact when compared to traditional chemical processes; this can be beneficial in improvising the selectivity and tolerability for sensitive functional groups.[7]

Thus, employing this technique would eliminate or minimize the use of toxic oxidizing/reducing agents and eliminate/minimize waste generation compared to conventional synthetic procedures, thus making it an eco-friendly and cost-effective method.

As the world shifts towards sustainable energy sources, electrochemical methods align well with renewable energy inputs, such as solar and wind power, making the whole synthetic process environmentally friendly.

Electrochemical methods are employed for forming carbon-carbon (C–C) and carbon-hetero (C–X) bonds, essential for constructing complex organic molecules. [8–10] It allows for the selective functionalization of organic compounds and enables the introduction of specific groups in a controlled manner. Also, it has found applications in the pharmaceutical industry, contributing to developing new drug candidates and modifying existing pharmaceuticals. The field extends to synthesizing organic materials, such as polymers and conducting polymers, with tailored properties for various applications.

In this context, our laboratory in the Department of Chemistry, IIT Hyderabad, is actively developing new synthetic processes based on environmentally friendly and cost-effective methods and extending their application in pharmaceutically relevant compounds.

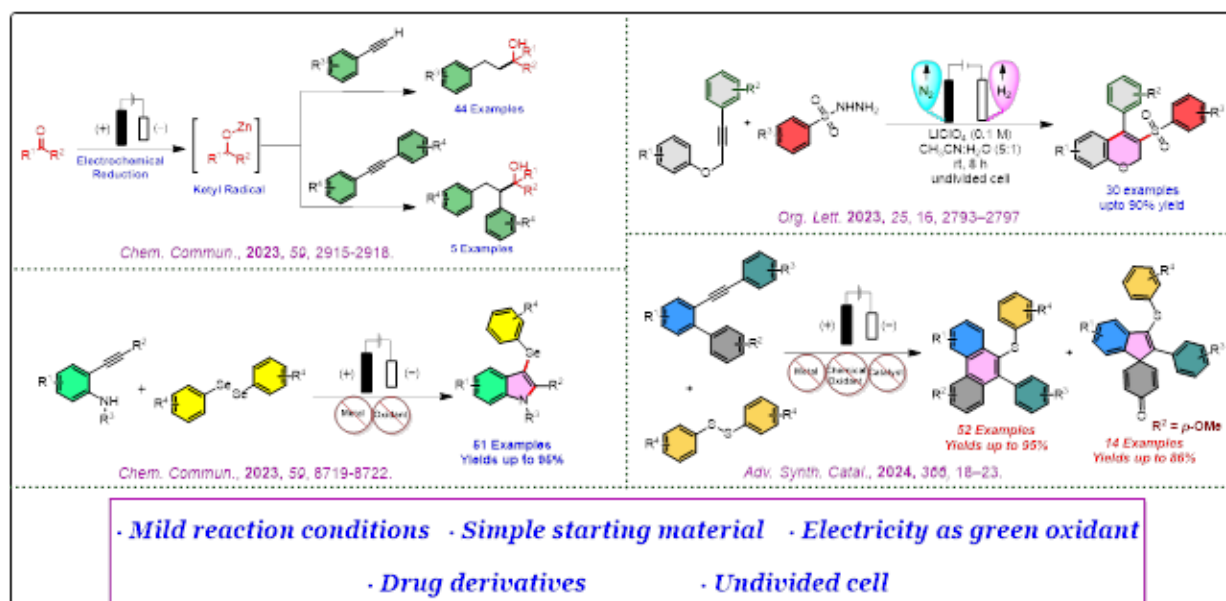


Figure-1: Transformative Organic Synthesis Through Electrochemical Marvels

For instance, our successful synthesis of tert-Alcohols, [11] 3-Selenylindoles, [12] Sulfonated 2H-Chromenes, [13] Fused Sulfenyl Phenanthrenes, and Sulfenyl Spiro Cyclohexa[4.5]trienones [14] relied on sustainable methods (Figure-1). These protocols work under mild reaction conditions at ambient temperature, utilizing constant current electrolysis in an undivided cell without utilizing external oxidants, reductants, or catalysts. We are currently focusing our research on overcoming challenges and optimizing these methods for widespread use in the chemical industry.

In conclusion, electrochemical organic synthesis would pave the way for its widespread adoption and open new possibilities for sustainable and efficient chemical transformations in organic synthesis and its applications across various fields. As research in this field continues, it will likely yield innovative solutions in achieving complex organic compounds with reduced environmental impact.

Reference:

- [1] C Kingston, M D Palkowitz, Y Takahira, J C Vantourout, B K Peters, Y Kawamata and P S Baran, *Acc Chem Res.*, 2020, 53, 72–83.
 [2] J E Nutting, J B Gerken, A G Stamoulis, D L Bruns and S S Stahl, *J Org Chem.* 2021, 86, 15875–15885.
 [3] Robert Francke and R Daniel Little, *Chem Soc Rev.*, 2014, 43, 2492–2521.
 [4] M Yan, Y Kawamata and P S Baran, *Chem Rev.*, 2017, 117, 13230–13319.
 [5] K Mahanty, D Maiti and S De Sarkar, *J Org Chem.* 2020, 85, 3699–3708.
 [6] Y Wang, S Dana, H Long, Y Xu, Y Li, N Kaplaneris and L Ackermann, *Chem Rev.* 2023, 123, 11269–11335.
 [7] Y Kawamata, K Hayashi, E Carlson, S Shaji, D Waldmann, B J Simmons, J T Edwards, C W Zapf, M Saito and P S Baran, *J Am Chem Soc.* 2021, 143, 16580–16588.
 [8] Y Kawamata, J C Vantourout, D P Hickey, P Bai, L Chen, Q. Hou, W Qiao, K Barman, M A Edwards, A F Garrido-Castro, J N de Gruyter, H Nakamura, K Knouse, C Qin, K J Clay, D Bao, C Li, J T Starr, C Garcia-Irizarry, N Sach, H S White, M Neurock, S D Minter and P S Baran, *J Am Chem Soc.* 2019, 141, 6392–6402.
 [9] T Sheng, H-J Zhang, M Shang, C He, Julien C Vantourout and Phil S Baran, *Org Lett.* 2020, 22, 7594–7598.
 [10] R Kumar, N Banerjee, P Kumar and P Banerjee, *Chem Eur J.* 2023, 29, e202301594.
 [11] A B Dapkekar and G Satyanarayana, *Chem Commun.* 2023, 59, 2915–2918.
 [12] A B Dapkekar and G Satyanarayana, *Chem Commun.* 2023, 59, 8719–8722.
 [13] J R Thondur, D S Sharada and G Satyanarayana, *Org Lett.* 2023, 25, 2793–2797.
 [14] A Balajirao Dapkekar, J Naveen and G Satyanarayana, *Adv Synth Catal.* 2024, 366, 18–23.

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Elucidating the facet dependence for solvent-mediated furfural acetalization reaction on Pd nanostructures

KID: 20230410

Structure-sensitive reactions are well known in heterogeneous catalysis and surface science wherein particle-size and shape-dependent catalytic activity and selectivity control is observed with nanoparticle systems. The size-dependent structure sensitivity arises due to the change in the proportion of the type of surface atoms (viz terrace, corner, or edge) with size. As the size increases, the fraction of terrace sites increases at the expense of edge or corner sites which is reflected in reactivity. Another parameter could be particle morphology, wherein particles with differently exposed facets show different reactivity. In addition to the structural and morphological effects, the performance of a catalyst is strongly affected by solvent properties such as polarity, basicity or proticity; therefore, finding the right solvent for a catalytic reaction is important.

In this context, the structure-sensitive behaviour and solvent effect towards an important reaction for the production of biofuels was investigated in the present study. Furfural dialkyl acetals (FDA) obtained from the acetalization of biomass-derived furfural (Figure-1) are promising biofuels because of their high calorific value and oxidation resistance. Using defined experiments (in collaboration with Dr. C.P. Vinod's Group at NCL Pune) and density functional theory (DFT) simulations, the structure-dependent activity and selectivity for furfural acetalization reaction in the presence of alcohols (methanol, ethanol, propanol and butanol) as solvents were studied over well-defined supported Pd nanostructures (octahedra (111), cubes (100) and spheres (both (111) and (100)) (Figure-2).

