

ELECTROCHEMICALLY MEDIATED OXIDATIVE C-C AND C-HET COUPLING

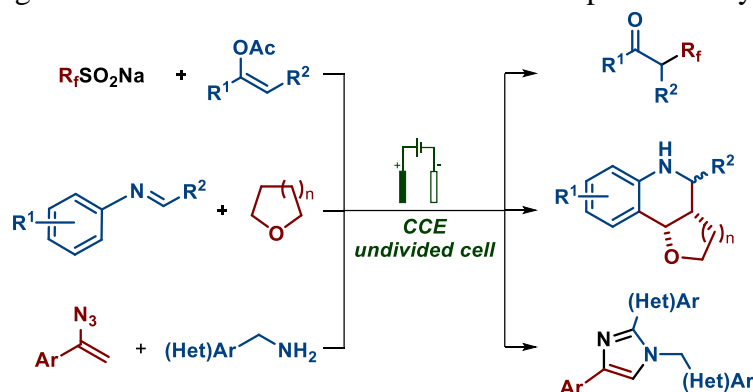
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Nowadays, electroorganic synthesis is considered as one of the most actively developing areas of modern organic chemistry. This study develops state-of-the-art synthetic organic electrochemistry – methods for C-C and C-Het bonds formation.

The electrochemical synthesis of fluorinated ketones from enol acetates and R_fSO_2Na in an undivided cell under constant current conditions was developed.¹ The electrosynthesis proceeded *via* perfluoroalkyl radical generation from sodium perfluoroalkyl sulfinate followed by addition to the enol acetate and transformation of the resulting C radical to a fluorinated ketone. The method is applicable to a wide range of enol acetates and results in the desired products in yields of 20 to 85%.



We disclosed the electrochemical synthesis of cyclic ether-annulated tetrahydroquinolines from imines and cyclic ethers.² The electrosynthesis proceeds *via* the enol ether formation from ethers following the aza-Diels-Alder [4+2] cycloaddition. The non-obviousness of the discovered process is due to the fact that cyclic ethers, common solvents for electrochemistry, are oxidized into enol ethers while the electrochemically labile imines must wait for the formation of a partner for cycloaddition while remaining unconsumed. Synthesized cyclic ether-annulated tetrahydroquinolines exhibit high antifungal activity, which is superior to the commercial fungicide Triadimefon.

Also, an electrochemically induced synthesis of imidazoles from vinyl azides and benzyl amines was reported.³ The discovered transformation is a multistep process whose main steps include the generation of electrophilic iodine species, 2*H*-azirine formation from the vinyl azide, followed by its reactions with benzyl amine and with imine generated from benzyl amine. The cyclization and aromatization of the obtained intermediate lead to the target imidazole. Despite possible cathodic reduction of various unsaturated intermediates with C=N bonds, the efficient electrochemically induced synthesis of imidazoles was carried out.

References

1. Electrochemical synthesis of fluorinated ketones from enol acetates and sodium perfluoroalkyl sulfinate / V.A. Vil', V.M. Merkulova, A.I. Ilovaisky [et al.] // *Org. Lett.* – 2021. – V. 23, – P. 5107–5112.
 2. Electrochemical synthesis of tetrahydroquinolines from imines and cyclic ethers *via* oxidation/aza-Diels-Alder cycloaddition / V.A. Vil', S.S. Grishin, E.P. Baberkina [et al.] // *Adv. Synth. Catal.* – 2022. – V. 364, – P. 1098–1108.
- V.A. Vil' Electrochemically induced synthesis of imidazoles from vinyl azides and benzyl amines / V.A. Vil', S.S. Grishin, A.O. Terent'ev // *Molecules.* – 2022. – V. 27. – P. 7721.