## TRIPLE-ROLE PROTIC IONIC LIQUIDS AS AN EMERGING TOOL IN ORGANIC SYNTHESIS

I.A. Andreev<sup>1</sup>, N.K. Ratmanova<sup>1</sup>, O.A. Ivanova<sup>2</sup>, I.V. Trushkov<sup>1, 3</sup>

<sup>1</sup>Laboratory of Chemical Synthesis, Dmitry Rogachev National Medical Research

Center of Pediatric Hematology, Oncology and Immunology,

Samory Mashela str., 1, Moscow, 117997, Russia;

<sup>2</sup> M.V. Lomonosov Moscow State University, Department of Chemistry,

Leninskie gory, 1-3, Moscow, 119991, Russia;

<sup>3</sup>N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,

Leninsky pr., 47, Moscow, 119991, Russia.

E-mail: ivan. and reev @fccho-moscow.ru

Modern demands of synthetic chemistry require the selection of reaction conditions, providing both high yields of the target products due to high chemo-, regio-, and stereoselectivity and conformity with the fundamental principles of green chemistry. Using protic ionic liquids (PILs), *i.e.*, low-melting salts of Brønsted acid and base, is an attractive solution to these challenges.

Recently, we proposed a novel concept of triple-role PILs in organic synthesis, *i.e.*, a solvent, an acid catalyst, and a reagent – a source of a nucleophile. We demonstrated the efficiency of this concept in the nucleophilic ring-opening of donor-acceptor (DA) cyclopropanes applying 1-methylimidazolium thiocyanate PIL<sup>1</sup>. We found unusual chemoselectivity of the ambident thiocyanate ion for this process; 3,5-disubstituted pyrrolidine-2-thiones – products of the formal (3+2)-cycloaddition of DA cyclopropanes with isothiocyanic acid – were formed exclusively.



## Triple Role of Protic Ionic Liquid

Then, the scope of this emerging concept was expanded on other classes of organic substrates. For this purpose, we varied reaction conditions, a base<sup>2</sup> and anionic<sup>3</sup> part of PIL.

## References

1. Protic ionic liquid as reagent, catalyst, and solvent: 1-methylimidazolium thiocyanate / I.A. Andreev, N.K. Ratmanova, A.U. Augustin [et al.] // Angew. Chem. Int. Ed. -2021. - Vol. 60, Iss. 14. - P. 7927–7934.

2. Triple role of thiocyanate-containing protic ionic liquids in chemodivergent ring-opening of 1,3-indanedione-derived donor-acceptor cyclopropanes / I.A. Andreev, N.K. Ratmanova, V.A. Shcherbinin [et al.] // in press.

3. 4-(Dimethylamino)pyridinium azide in protic ionic liquid media as a stable equivalent of hydrazoic acid / I.A. Andreev, M.A. Boichenko, N.K. Ratmanova [et al.] // Adv. Synth. Catal. – 2022. – Vol. 364, Iss. 14. – P. 2403–2415.

This work was supported by the Russian Science Foundation, project # 21-73-10212.

<sup>©</sup> Andreev I.A., Ratmanova N.K., Ivanova O.A., Trushkov I.V., 2023