

THIOCYANATE-CONTAINING PROTIC IONIC LIQUIDS IN RING-OPENING OF 1,3-INDANEDIONE-DERIVED DONOR-ACCEPTOR CYCLOPROPANES

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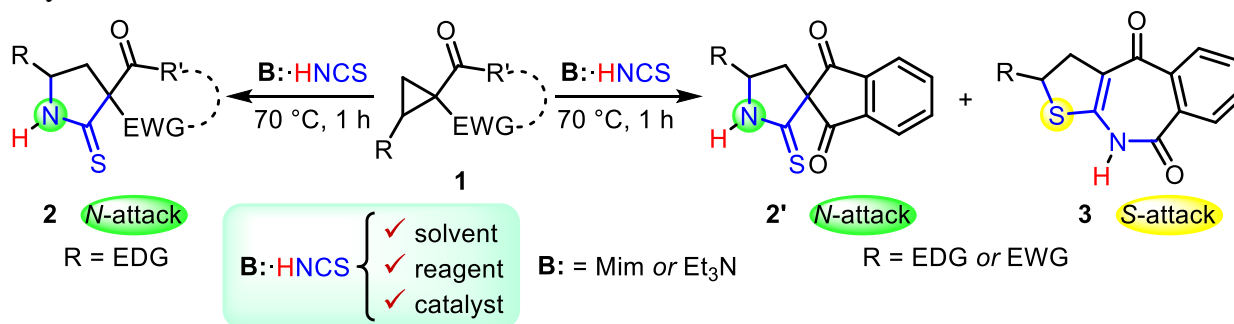
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Protic ionic liquids (PILs) – low-melting salts of Brønsted acid and base – have found their application in different areas and are promising green alternatives to traditional chemicals due to their ability to dissolve both hydrophobic and hydrophilic molecules, negligible vapour pressure, thermal stability, and ease of recovery. Recently, we proposed a novel concept of the triple role of PILs with nucleophilic anions in organic synthesis, *i.e.*, a solvent, an acid catalyst, and a reagent – a source of a nucleophile. The efficiency of this concept was demonstrated in the ring-opening of ester-derived donor-acceptor (DA) cyclopropanes **1** in thiocyanate-containing PILs, affording pyrrolidine-2-thiones **2** – products of *N*-attack – exclusively¹.

Next, we transferred the triple role PILs concept onto 1,3-indanedione-derived DA cyclopropanes **1**, which are more reactive than the corresponding dicarboxylates due to the *spiro*-activation. Heating of DA cyclopropanes **1** in thiocyanate-containing PILs resulted in chemodivergent domino transformations affording unknown thieno[2,3-*c*][2]benzazepines **3** (products of *S*-attack) and/or unusual spiro[2-thioxopyrrolidine-3,2'-indane-1',3'-diones] **2'** (products of *N*-attack). In 1-methylimidazolium thiocyanate, both products **2'** and **3** were formed in a ratio depending on the nature of the R-substituent in the starting cyclopropane **1**. On the contrary, treating the same substrates with triethylammonium thiocyanate resulted in spiro[2-thioxopyrrolidine-3,2'-indane-1',3'-diones] **2'** exclusively.



The designed transformation is the first example of the process chemoselectivity switching by a simple variation of a base part of a protic ionic liquid. In all these processes, PILs serve in concert as a reaction medium, a source of the proton providing a general acid catalysis, and the nucleophile².

References

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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.

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