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BOOK OF ABSTRACTS

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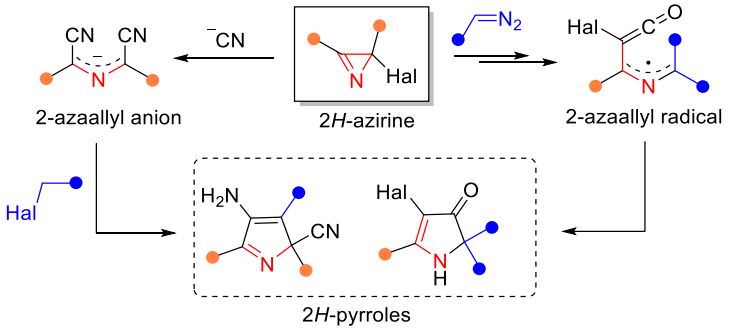
2-Azaallyl anions and 2-azaallyl radicals from 2*H*-azirines on the way to 2*H*-pyrroles

Novikov M.S., Agafonova A.V., Pavlenko J.I.

Saint Petersburg State University, Institute of Chemistry,
199034 Saint Petersburg, 7/9 Universitetskaya nab.
e-mail: m.novikov@spbu.ru

Intermolecular domino-reactions of 2*H*-azirines with carbon-centered nucleophiles and electrophiles, proceeding through the cleavage of one of three bonds of the ring, serve as a powerful tool for the construction of a variety of 5-membered heterocycles, including 1*H*- and 3*H*-pyrroles, 1*H*- and 2*H*-imidazoles, 2*H*-1,2,3-triazoles, oxazoles, thiazoles, and furan-2(5*H*)-ones [1, 2]. Another scenario for the two-atom azirine ring expansion, examples of which are still rare, involves a two-step procedure "azirine ring opening into a stable acyclic intermediate/heterocyclization". One of the advantages of this approach is the ability to fine tune the reaction conditions to achieve high regio- and stereoselectivity of the cyclization step. The report discusses the prospects of using this approach to the synthesis of new 2*H*-pyrrole derivatives. Two conceptually different solutions to this problem are proposed, one of which involves the pre-synthesis of 2-azalyl anion salts as stable acyclic intermediates, precursors of the final 4-amino-2*H*-pyrroles [3]. The second version of the 2*H*-pyrrole core formation is focused on the generation and "unfavorable" anti-Baldwin 5-*endo-trig* cyclization of 2-azaallyl radicals. The synthetic potential and limitations of both methods are discussed, as well as the results of experimental and quantum chemical studies of the reaction mechanisms.



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