

Catalytic Anomeric Based Oxidation

Compiled by Meysam Yarie

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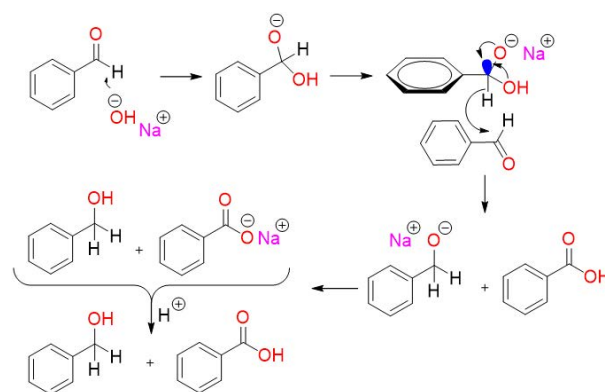
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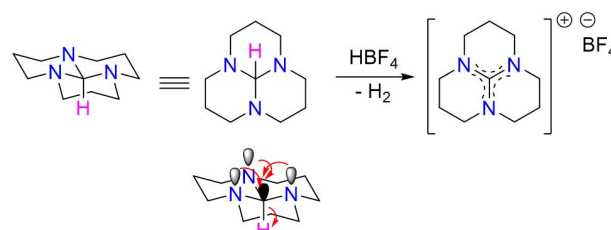
This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

Anomeric effect has found its influential position in the field of chemistry and it can be defined as stereoelectronic stabilizing effect that favor the placement of electronegative substituents in the axial, rather than equatorial, position in a pyranoid ring system at C1 [1]. Subsequent studies show that the anomeric effect is not restricted to carbohydrate chemistry, and it represents the explanation for varied chemical phenomena. The impact and trace of anomeric effect can be found in priority of gauche positions over anti orientation in Newman projections [1], stereochemical selectivities in radical reactions and also in other conformational precedences [2]. Recent explorations have revealed that the anomeric effect play an effective role in the activation and fixation of small molecules at the carbene site of *N*-heterocyclic carbenes [3]. Furthermore, in the Cannizzaro reaction the anomeric effect, through the interfering in the reaction mechanism caused the unusual hydride transfer in the way for the target molecule generation (Scheme 1) [4].



Scheme 1. Hydride transfer in mechanism of Cannizzaro reaction through anomeric effect.



Scheme 2. Anomeric effect causes to hydrogen releasing from the tricyclic orthoamide

Another privileged example for the role of anomeric effect in the mechanistic aspect of the reaction is in the case of tricyclic orthoamide as a driving force for the releasing of H₂ molecule (Scheme 2) [4].

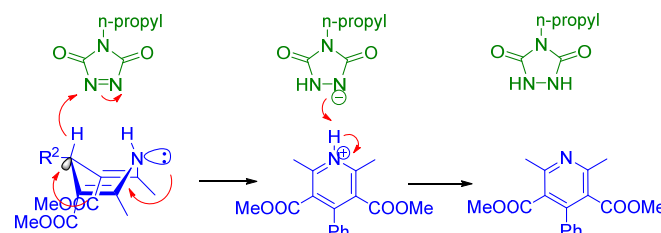
Recently, Zolfigol *et al.* have introduced a new mechanistic outlook for the oxidative aromatization of some heterocyclic compounds based on anomeric effect and present the term of “anomeric based

oxidation (ABO)” as an explanation for the final step of aromatization mechanism [4-11].

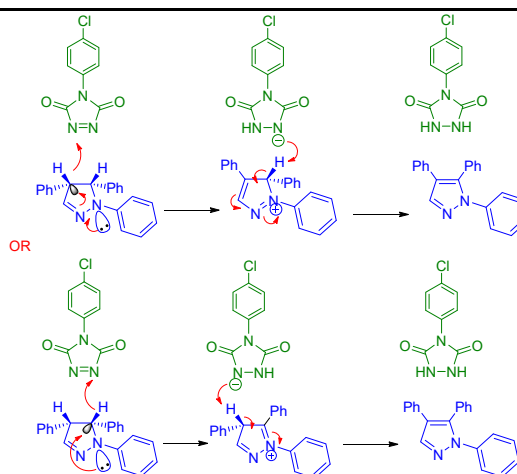
In this spotlight, I have tried to do my duty for expanding the new established term entitled “anomeric based oxidation” and collect the obtained results from their experimental and computational investigations under the name of “catalytic anomeric based oxidation”.

Abstracts

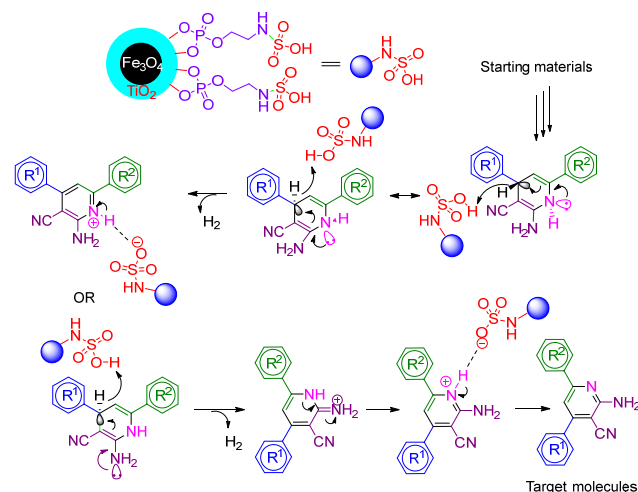
(A) The computational investigation of aromatization of 1,4-dihydropyridines using 1,2,4-triazolinedione as oxidizing agent show that the stepwise ABO mechanism dominated the common concerted oxidation via the hydrogen abstraction-addition mechanism [4].



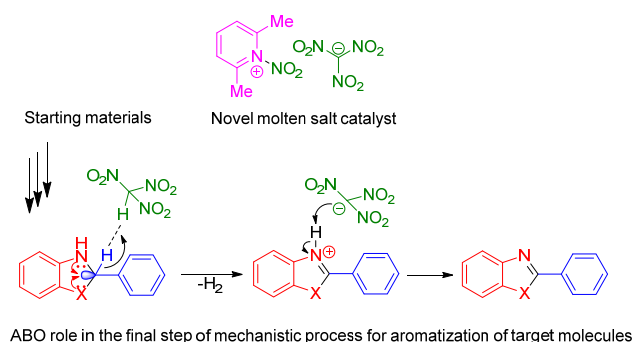
(B) Another computational investigation have revealed that in the case of aromatization of 1,3,5-trisubstituted pyrazolines and using 1,2,4-triazolinedione as oxidizing agent, the stepwise ABO mechanism dominated the common concerted oxidation *via* the hydrogen abstraction-addition mechanism [4].



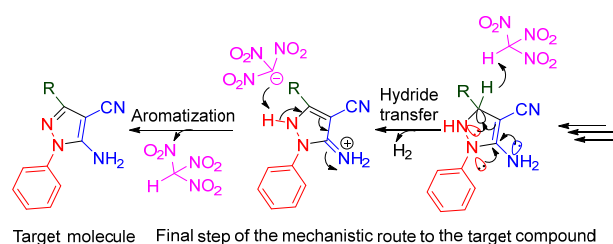
(C) The catalytic activity of the Fe₃O₄@TiO₂@O₂PO₂(CH₂)NHSO₃H, as a nanomagnetic heterogeneous core-shell catalyst was successfully explored for the synthesis of 2-amino-4,6-diphenylnicotinonitrile derivatives under mild and solvent free conditions. The suggested plausible mechanism presents an anomeric based oxidation pathway to the target materials in the final step of the synthetic process [5]. Also, the same team, present the experimental and theoretical studies of the nanostructured {Fe₃O₄@SiO₂@(CH₂)₃Im}C(CN)₃ catalyst for 2-amino-3-cyanopyridine preparation *via* an anomeric based oxidation [6].



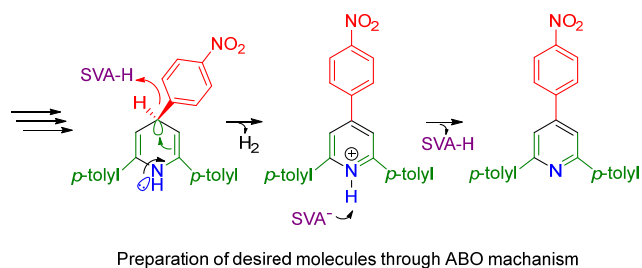
(D) [2,6-DMPy-NO₂]⁺C(NO₂)₃⁻ as a new molten salt catalyst represent a robust catalytic applicability at the synthesis of 2-substituted benz-(imida, oxa and othia)-zole derivatives under green reaction profile. The achieved data indicated that the both of the experimental and theoretical investigation confirm the role of new established idea namely “anomeric based oxidation” in the final step of the reaction mechanism to the desired molecules [7].



(E) In 2015, Zolfigol *et al.* have presented an anomeric based oxidation mechanism for the final step of the mechanistic process for the synthesis of 1,4-dihydropyridino-[2,3-*c*]-pyrazole derivatives. Furthermore, the jointed computational study verified the obtained results from experimental exploration [8]. Also, it is demonstrated that dioxomolybdenum complex supported on silica-coated magnetite nanoparticles can act as an effective catalyst for the synthesis of pyrazole derivatives *via* anomeric based oxidation mechanism [9].



(F) In another investigation, the aromatization of 1,4-dihydropyridines as intermediates in the way for the synthesis of corresponding pyridine derivatives were inspected using silica vanadic acid as reaction promoter. The experimental and computational inspections have revealed that the anomeric based oxidation (ABO) mechanism play a crucial role in the final step of the mechanistic pathway [10]. Also, Moosavi-Zare and co-workers, have been applied trityl chloride as a organocatalyst for the preparation of 2,4,6-triarylpyridines *via* anomeric based oxidation [11].



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