Iranian Journal of Catalysis Spotlight 10(1), 2020, 79-83

IRANIAN JOURNAL OF CATALYSIS

Catalytic vinylogous anomeric based oxidation (Part I)

Compiled by Meysam Yarie

Meysam Yarie was born in 1987 in Malayer/ Hamedan, Iran. He received his B.Sc. in Applied Chemistry from Malek-Ashtar University of Technology and M.Sc. in Organic Chemistry from Kurdistan University under the supervision of Dr. Kamal Amani. He received his Ph.D. from Bu-Ali Sina University under the supervision of Professor Mohammad Ali Zolfigol. He is currently working towards his Post-Doctoral under the supervision of Professor Mohammad Ali Zolfigol at Bu-Ali Sina University. His research interest is the design, synthesis, characterization and applications of task-specific catalysts, ionic liquids and molten salts in the organic synthesis.

Faculty of Chemistry, Bu-Ali Sina University, Hamedan 6517838683, Iran.

E-mail: myari.5266@gmail.com

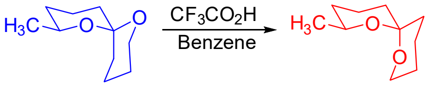
This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

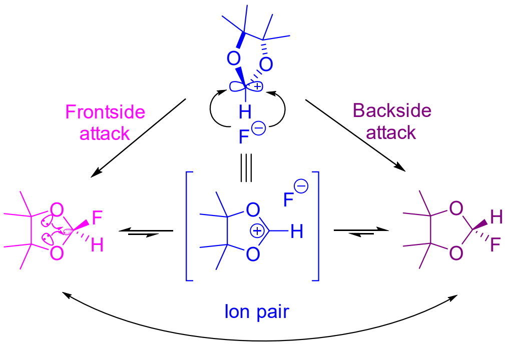
Stereoelectronic effects is a bridge between structure and reactivity [1]. Anomeric effect plays an important role in the domain of stereoelectronic interaction and can be used for description of several unusual phenomena. Intramolecular negative hyperconjugation is also known as anomeric effect [2]. In anomeric effect, both donor (lone pairs) and acceptor groups (electronegative elements) coexist in a proper molecule. This coexistence causes the acceptor groups to prefer the axial position in anomeric position (Scheme 1) [1, 3-15].

Another fascination example of the role of anomeric effect for justifying unusual phenomena is depicted in the scheme 2. Dynamic nuclear magnetic resonance study of 2-fluoro-4,4,5,5-tetramethyl-1,3-dioxole, reveals hidden iconicity. In the case of this compound, anomeric interaction of oxygen lone pairs with antibonding orbital of C-F ($n_O \rightarrow \sigma^*_{C\text{-}F}$) results in a rapid shift of the fluorine atom from one side of the molecule to another one [16].

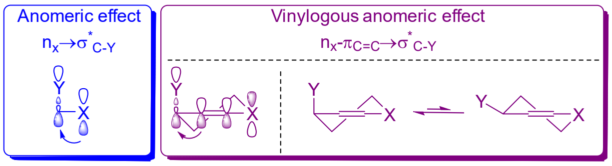
Vinylogous anomeric effect is one of the influential subclasses of the anomeric effect. As it can be seen in the scheme 3, if anomeric interactions transmitted through a double bond, it has been called vinylogous anomeric effect [1, 17-19].



Scheme 1. Acceptor group prefer the axial position in anomeric position.

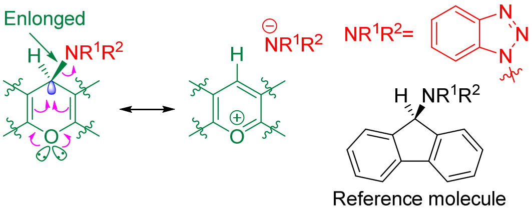


Scheme 2. Hidden iconicity in 2-fluoro-4,4,5,5-tetramethyl-1,3-dioxole due to the existence of anomeric effect.



Scheme 3. General modes of anomeric effect and vinylogous anomeric effect.

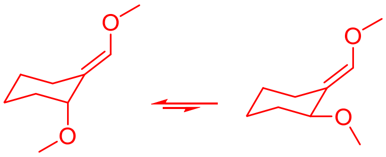
By using X-ray crystallography Katritzky and coworkers, they had investigated the structural consequences of vinylogous anomeric effect. The obtained data show that the existence of this phenomenon resulted in elongation of C-N bond in exocyclic benzotriazole substituent compare with a C-N bond of the reference molecule without oxygen (Scheme 4) [19].



Scheme 4. Structural outcomes of the vinylogous anomeric effect.

Also, it is suggested that vinylogous anomeric effect can be operated with exocyclic π-systems such as alkenes and ketoximes. For example, in the case of below alkene, the equilibrium is towards the structure in which methoxy group occupies the axial position [1].

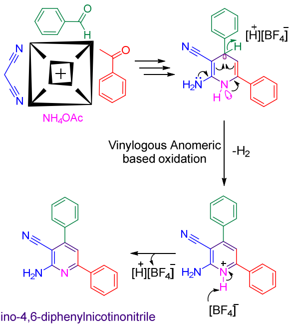
The main goal of this spotlight, is to highlight and expand the new term of "vinylogous anomeric based oxidation" which driven from vinylogous anomeric effect.



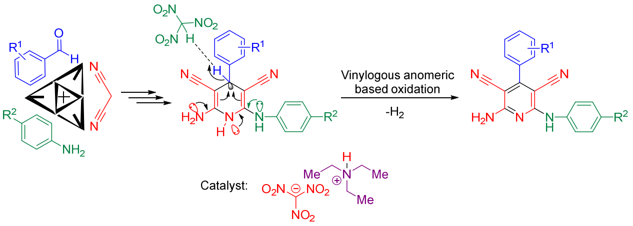
Scheme 5. Vinylogous anomeric effect with the exocyclic π-system.

Abstracts

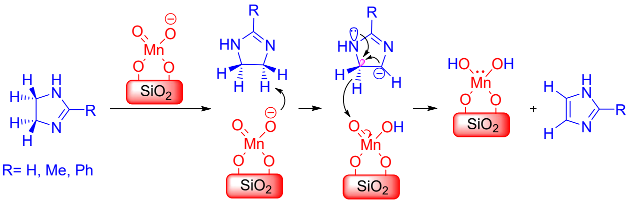
(A) In 2017, Zolfigol and co-workers, have been reported the application of HBF_4 as an oxidizing promoter catalyst for the preparation of 2-amino-4,6-diphenylnicotinonitrile. In the reported work, experimental and theoretical supported the vinylogous anomeric based oxidation mechanism for the synthesis of target molecule [2, 20-21].



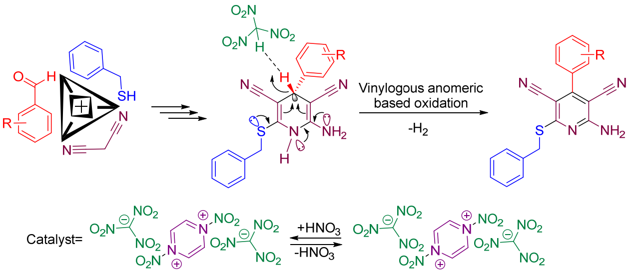
(B) In another investigation, Zolfigol *et al.,* have been reported the synthesis and characterization of triethylammonium based ionic liquid and molten salt. They have applied the titled catalysts for the preparation of pyridine-3,5-dicarbonitrile derivatives through an one-pot three-component protocol via a vinylogous anomeric based oxidation manner [22].



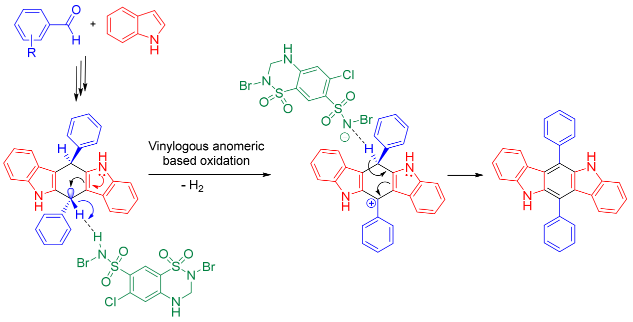
(C) Taherpour *et al.*, have been reported the computational study of 2-substituted imidazoline derivatives oxidation to the corresponding imidazoles using silica gel modified by potassium permanganate ($KMnO_4$/ SiO_2). Their obtained data from computational study (DFTB3LYP/6-31G** method) disclosed that reaction proceeds *via* stepwise *E1cb'* mechanism on the basis of the anomeric effect [23].



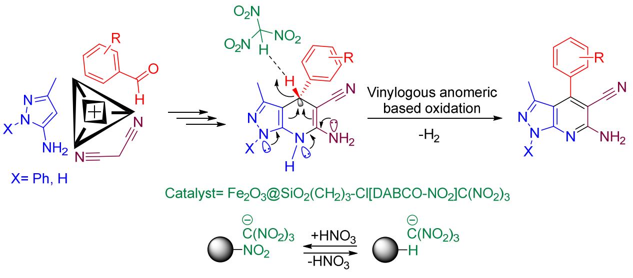
(D) After design, synthesis and fully characterization, $\{[1,4\text{-pyrazine-}NO_2][C(NO_2)_3]_2\}$ has been showed high catalytic performance towards the synthesis of 2-amino-3,5-dicarbonitrile-6-sulfanylpyridine derivatives through the reaction of aromatic aldehydes, malononitrile and benzyl mercaptane under mild reaction conditions. Also, experimental and theoretical investigations, suggested a plausible mechanistic pathway via a vinylogous anomeric based oxidation mechanism for the synthesis of desired products [24].



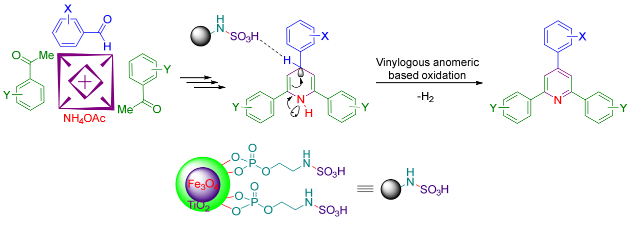
(E) In 2018, an efficient and novel protocol have been reported for the synthesis of indolo [3,2-*b*]carbazole derivatives by using *N*,2-dibromo-6-chloro-3,4-dihydro 2*H*-benzo[*e*][1,2,4]thiadiazine-7-sulfonamide-1,1-dioxide as catalyst. Both experimental and computational investigations suggested a plausible vinylogous anomeric based oxidation mechanism for the synthesis of indolo [3,2-*b*]carbazoles [25].



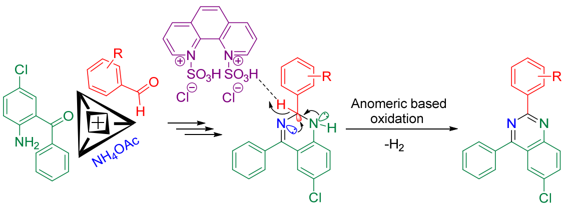
(F) In a separate study, $Fe_2O_3@SiO_2(CH_2)_3\text{-}Cl[DABCO\text{-}NO_2]C(NO_2)_3$ as a novel nanomagnetic catalyst has been designed, synthesized and fully characterized by proper techniques. Then, the titled catalyst has been used as a recyclable catalyst for the preparation of 3-methyl-1-phenyl-1*H*-pyrazol-5-amine and/or 3-methyl-1*H*-pyrazol-5-amine through a one-pot three component reaction via a vinylogous anomeric based oxidation process [26].



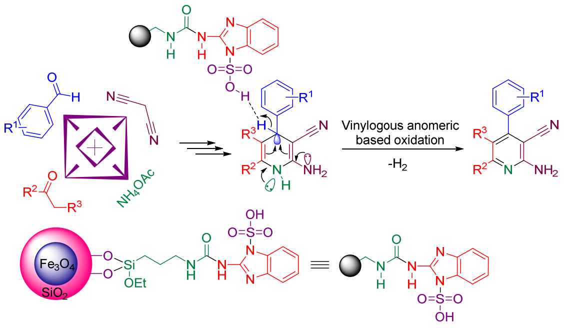
(G) In 2018, a green and efficient procedure have been developed for the synthesis of 2,4,6-triarylpyridines. The authors have been applied sulfonic acid-functionalized titana-coated magnetic nanoparticles as catalyst and suggested a vinylogous anomeric based oxidation mechanism for the synthesis of target molecules [27]. Also, in the another work, chitosan supported vanadium oxo have been synthesized and applied as catalyst at the preparation of 2,4,6-triarylpyridines via a vinylogous anomeric based oxidation [28].



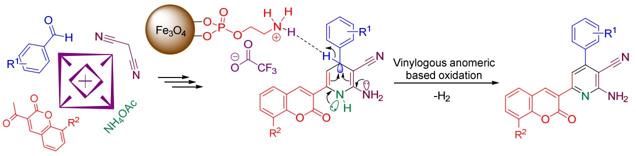
(H) $[Phen(SO_3H)_2]Cl_2$ has been prepared by the reaction of 1,10-Phenanthroline and $ClSO_3H$ and applied as recoverable catalyst for the synthesis of *N*-*h*eterocycle compounds *via* anomeric based oxidation mechanism [29].



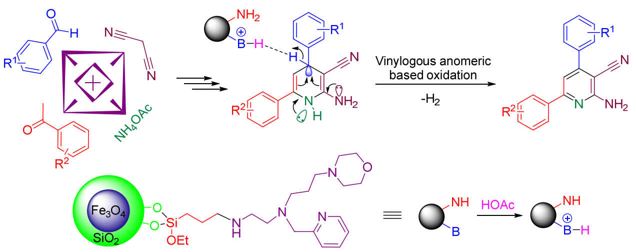
(I) In 2019, Zolfigol *et al.,* have reported the synthesis of a new nano magnetic catalyst bearing urea linker namely $Fe_3O_4@SiO_2@(CH_2)_3$-urea-benzimidazole sulfonic acid. After, fully characterization, the title catalyst has been used for the preparation of 2-amino-3-cyano pyridine derivatives through a vinylogous anomeric based oxidation pathway [30].



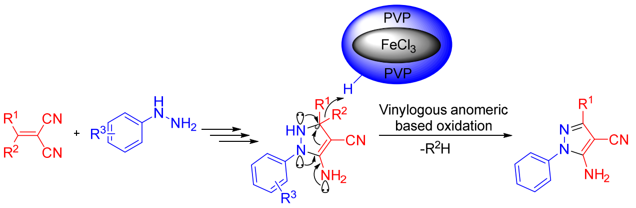
(J) An ionically tagged nano magnetic catalyst bearing phosphate spacer has been synthesized and characterized. The resulting structure has been applied as a reusable catalyst for the synthesis of chromene-linked nicotinonitrile derivatives under solvent free conditions *via* a vinylogous anomeric based oxidation protocol [31].



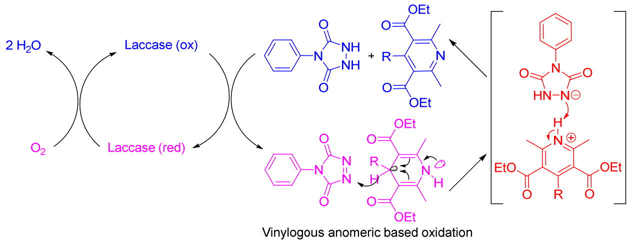
(K) In the another investigation, a novel magnetic nanoparticles bearing morpholine tags have been synthesized, characterized and applied as a recoverable catalyst for the synthesis of 2-amino-4,6-diphenylnicotinonitrile derivatives. The authors have been suggested a vinylogous anomeric based oxidation mechanistic pathway for the synthesis of target molecules [32].



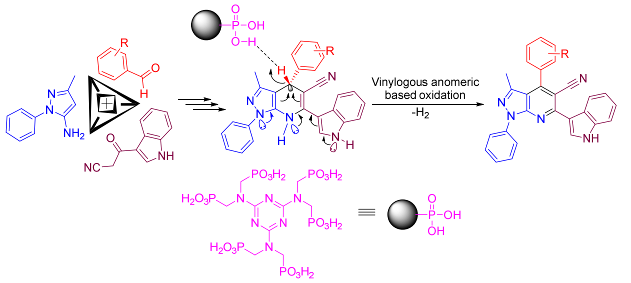
(L) In 2019, Sarma and co-workers have been reported the synthesis of 5-amino-1*H*-pyrazole-4-carbonitrile derivatives in the presence of $FeCl_3$/PVP as homogeneous catalytic system through a vinylogous anomeric based oxidation mechanism [33]. Also, gelatoric ionic liquids have been applied for the synthesis of the title structures [34].



(M) In 2019, Rostami et al., have been reported the aerobic oxidative aromatization of Hantzsch 1,4-dihydropyridines to the corresponding pyridine derivatives *via* a vinylogous anomeric based oxidation mechanism. The authors have been applied the Laccase enzyme/4-Phenyl urazole as a cooperative catalytic oxidation system [35].



(N) In a separate study, Zolfigol and co-workers have been reported the synthesis of a novel nanostructured melamine based organo solid acid bearing phosphorus acid tags as an efficient catalyst for the synthesis of (3'-indolyl) pyrazolo[3,4-*b*]pyridine derivatives through the three component reaction under refluxing EtOH. Authors have been presented a vinylogous anomeric based oxidation mechanism for the synthesis of desired molecules [36].



References

[1] I.V. Alabugin, Stereoelectronic Effects: A Bridge Between Structure and Reactivity, Wiley, Hoboken, 2016.

[2] A.A. Taherpour, M.A. Zolfigol, J. Mol. Struct. 1179 (2019) 719-724.

[3] S.A. Glover, A.A. Rosser, A.A. Taherpour, B.W. Greatrex, Aus. J. Chem. 67 (2014) 507-520.

[4] D.P. Curran, N.A. Porter, B. Giese, Stereochemistry of radical reactions: concepts, guidelines, and synthetic applications, VCH, New York, 1995.

[5] V.F. Rudchenko, Chem. Rev. 93 (1993) 725-739.

[6] S.A. Glover, Tetrahedron 54 (1998) 7229-7271.

[7] S.A. Glover, A.A. Rosser, J. Phys. Org. Chem. 28 (2015) 215-222.

[8] H. Song, Y. Kim, J. Park, K. Kim, E. Lee, Synlett 27 (2016) 477-485.

[9] V.G.S. Box, J. Mol. Struct. 569 (2001) 167-178.

[10] E. Juaristi, G. Cuevas, Tetrahedron 48 (1992) 5019-5087.

[11] I.V. Alabugin. G.D.P. Gomes. M.A. Abdo, WIREs Comput. Mol. Sci. 9 (2018) e1389.

[12] I.V. Alabugin, K.M. Gilmore, P.W. Peterson, WIREs Comput. Mol. Sci. 1 (2011) 109-141.

[13] S.Z. Vatsadze, Y.D. Loginova, G.D.P. Gomes, I.V. Alabugin, Chem. Eur. J. 23 (2016) 3225-3254.

[14] Deslongchamps, P. Pure Appl. Chem. 65 (2009) 1161-1178.

[15] M. Yarie, Iran. J. Catal. Spotlight 7 (2017) 85-88.

[16] M. Oki, H. Ikeda, S. Toyota, Bull. Chem. Soc. Jpn. 72 (1999) 1343-1349.

[17] D.P. Curran, Y.G. Suh, Carbohydr. Res. 17 (1987) 161-191.

[18] (a) S.E. Denmark, M.S. Dappen, N.L. Sear, R.T. Jacobs, J. Am. Chem. Soc. 112 (1990) 3466-3474. (b) A. Nowacki, B. Liberek, Carbohydr. Res. 462 (2018) 13-27. (c) A. Nowacki, B. Liberek, Carbohydr. Res. 371 (2013) 1-7. (d) A. Nowacki, D. Walczak, B. Liberek, Carbohydr. Res. 352 (2012) 177-185. (e) M. Asgari, D. Nori-Shargh, Struct. Chem. 28 (2017) 1803-1814.

[19] A.R. Katritzky, P.J. Steel, S.N. Denisenko, Tetrahedron 57 (2001) 3309-3314.

[20] M.A. Zolfigol, M. Kiafar, M. Yarie, A.(A.) Taherpour, T. Fellowes, A. N. Hancok, A. Yari, J. Mol. Struct. 1137 (2017) 674-680.

[21] A.(A.) Taherpour, M.A. Zolfigol, RSC Adv. 7 (2017) 53617-53621.

[22] S. Baghery, M.A. Zolfigol, F. Maleki, New J. Chem. 41 (2017) 9276-9290.

[23] A.(A.) Taherpour, A. Yari, F. Ghasemhezaveh, M.A. Zolfigol, J. Iran. Chem. Soc. 14 (2017) 2485-2493.

[24] M.A. Zolfigol, M. Safaiee, B. Ebrahimghasri, S. Baghery, S. Alaie, M. Kiafar, A.(A.) Taherpour, Y. Bayat, A. Asgari, J. Iran. Chem. Soc. 14 (2017) 1839-1852.

[25] M.A. Zolfigol, A. Khazaei, F. Karimitabar, M. Hamidi, F. Maleki, B. Aghabarari, F. Sefat, M. Mozafari, J. Heterocycl. Chem. 55 (2018) 1061-1068.

[26] J. Afsar, M.A. Zolfigol, A. Khazaei, D.A. Alonso, A. Khoshnood, Y. Bayat, A. Asgari, Res. Chem. Intermed. 44 (2018) 7595-7618.

[27] M.A. Zolfigol, F. Karimi, M. Yarie, M. Torabi, Appl. Organometal. Chem. 32 (2018) e4063.

[28] M. Safaiee, B. Ebrahimghasri, M.A. Zolfigol, S. Baghery, A. Khoshnood, D.A. Alonso, New J. Chem. 42 (2018) 12539-12548.

[29] S. Babaee, M.A. Zolfigol, M. Zarei, J. Zamanian, ChemistrySelect 3 (2018) 8947-8954.

[30] M. Torabi, M. Yarie, M.A. Zolfigol, Appl. Organometal. Chem. 33 (2019) e4933.

[31] F. Karimi, M.A. Zolfigol, M. Yarie, Mol. Catal. 463 (2019) 20-29.

[32] S. Kalhor, M. Yarie, M. Rezaeivala, M.A. Zolfigol, 45 (2019) 3453-3480.

[33] H.M.F. Elnagdy, D. Sarma, ChemistrySelect 4 (2019) 783-787.

[34] S. Noura, M. Ghorbani, M. A. Zolfigol, M. Narimani, M. Yarie, M. Oftadeh, J. Mol. Liq. 271 (2018) 778-785.

[35] D. Khaledian, A. Rostami, S.A. Zarei, B. Mohammadi, J. Iran. Chem. Soc. 16 (2019) 1871-1878.

[36] J. Afsar, M. A. Zolfigol, A. Khazaei, M. Zarei, Y. Gu, D. A. Alonso, A. Khoshnood, Mol. Catal. 2019, doi: 10.1016/j.mcat.2019.110666.