IRANIAN JOURNAL OF CATALYSIS

Glycoluril based catalysts

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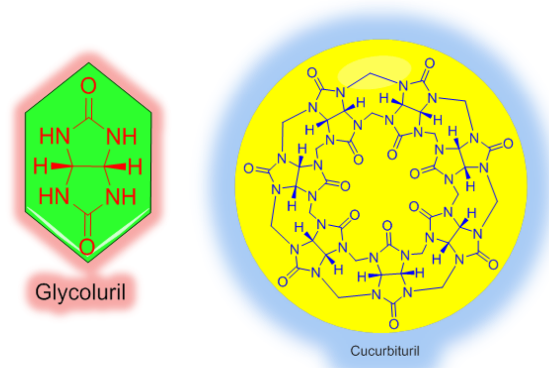
This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

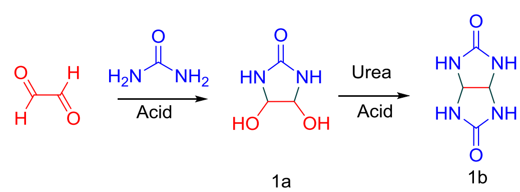
Glycoluril, a simple monomer consisting of four amidic nitrogens and two amidic carbonyl groups, was first synthesized by Schiff et al. in 1877 by the condensation reaction of urea and glyoxal in the presence of concentrate hydrochloric acid [1]. Glycoluril derivatives attract great attention of many researchers due to their functionalization and diverse practical applications [2]. Glycoluril derivatives have a wide spectrum of biological activities including anxiolytic, sedative, and nootropic effects [3]. This compound, as biological urea-based building blocks, have many applications in the organic and inorganic chemistry. Glycoluril as a simple heterobicyclic compound has been used for the synthesis of supramolecular hosts, molecular clips, cucurbiturils, energetic materials, propellanes, nitrogen fertilizers, ribbons, ditopic receptors and iodogen for the oxidation of urazoles. In addition, they have found many applications as catalyst in many chemical reactions (Scheme 1) [4].

Condensation reaction between urea and glyoxal under acidic conditions is known to yield diol 1a. While the same reaction under excessive amounts of urea leads to the formation of glycoluril (Scheme 2) [5].



Scheme 1. Structure of glycoluril and cucurbituril.

Condensation reaction of glycoluril and formaldehyde in concentrated hydrochloric acid leads to insoluble polymeric substance now known as Behrend's polymer.

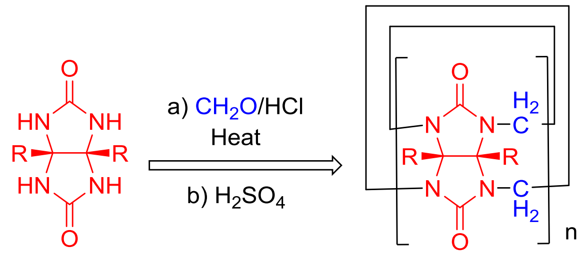


Scheme 2. Synthesis of glycoluril.

Behrend *et al*. reported the synthesis cucurbituril as a crystalline substance in good yield (40–70%) by recrystallization from concentrated H_2SO_4 [6].

One of the important usages of glycoluril and its derivatives, is the synthesis of organic catalysts. Glycoluril and its derivatives as organocatalysts have many advantages such as easily accessible, simple, and nontoxic organic molecules.

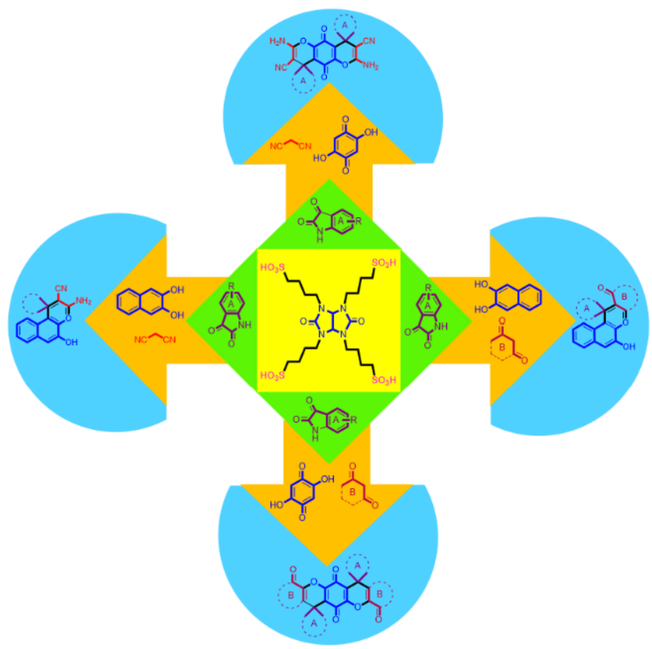
The family of this compound are used in different contexts as organocatalyst such as design and application of solid acids in the synthesis of organic compounds, various organic transformations through stable hydrogen bonding [1,7]. In this spotlight, due to interesting structural features of glycoluril and its derivatives, its versatility towards the synthesis of solid acids and organocatalysts for different goals in organic chemistry is highlighted.



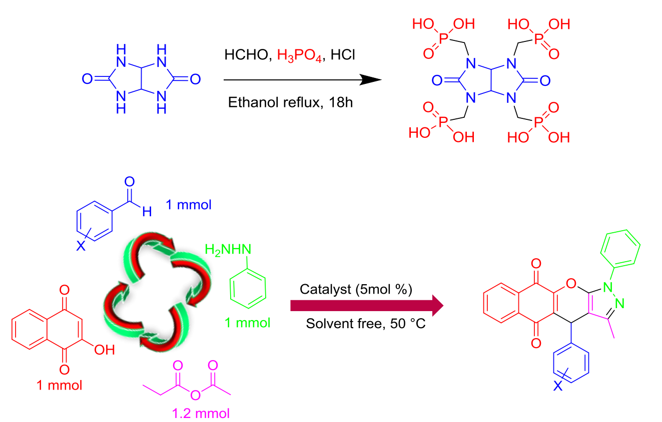
Scheme 3. Synthesis of cucurbituril.

Abstracts

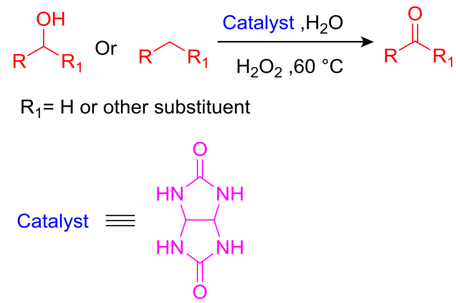
(A) In 2018, Zolfigol and co-workers, applied glycoluril based catalyst with sulfonic acid tags as a biological and reusable promoter for the synthesis of mono- and bis spiropyrans. The efficiency and reusability of the catalyst, and its generality, easy work-up, high yields, short reaction times and cleaner reaction profile are the major advantages of the described methodology [7].



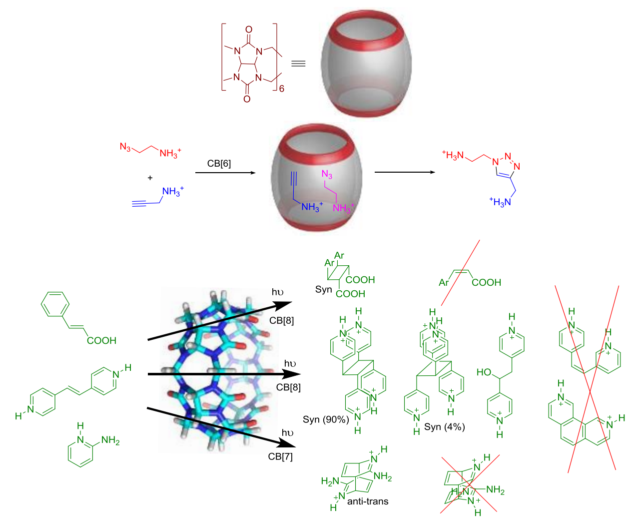
(B) In another work, Zolfigol and co-workers, reported the synthesis and characterization of a glycoluril based structure with phosphorous acid tags as a nanostructured catalyst. Then, they applied the resulting catalyst, in the synthesis of natural henna-based compounds. In this work, the preparation of a crabby biological based glycoluril tetrakis(methylene phosphorous acid) (GTMPA) was investigated for the first time. Two convenient methods for the synthesis of novel biological henna-based 3-methyl-1,4-diphenyl-1,4-dihydrobenzo [6,7] chromeno[2,3-c]pyrazole-5,10-diones were also reported in the presence of described nano catalyst [7].



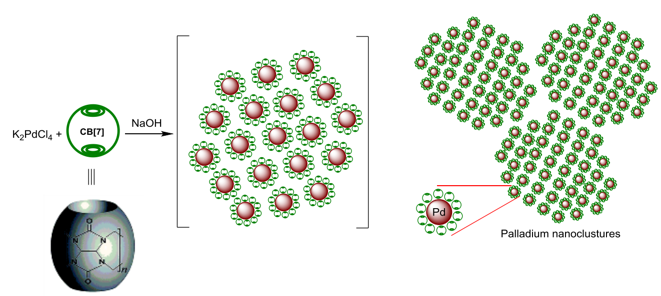
(C) In another work, glycoluril have been utilized as an organocatalyst for the direct oxidation of alcohols and benzylic sp^3 carbons to the corresponding carbonyls. Applied organocatalyst gave excellent conversion and selectivity of the products in an aqueous medium using 50% hydrogen peroxide at 60 °C [1].



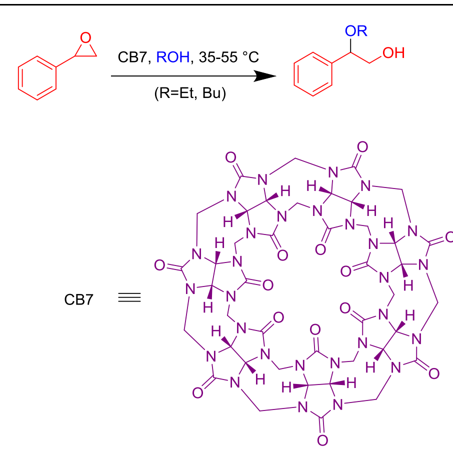
(D) Supramolecular nanoreactors are used in various interactions such as hydrogen bonding, electrostatic, van der Waals and p-p interactions steric effects, and so on. Among macrocycle compounds, the cucurbiturils applied in supramolecular nanoreactors for catalysis of Huisgen type 1,3-cycloaddition between ammonium-alkyne and ammonium-azide, and several photodimerizations. This compound has a good selectivity due to their cavities size [8].



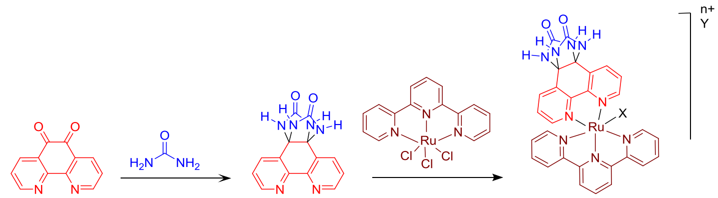
(E) One of the catalytic application of cucurbituril, is reduction of 4-nitrophenol with synthesis of honeycomb-like palladium nanostructures in water at room temperature. For the synthesis of palladium nanoparticles, an aqueous solution of K_2PdCl_4 was added to an equivalent amount of aqueous CB [7] at room temperature. The light brown-colored solid particles were obtained around 2h after the addition of NaOH to the resulting solution, indicating the formation of palladium nanoparticles [9].



(F) In a separate study, cucurbituril applied in catalytic alcoholysis of epoxides based on metal-free solids method. Cucurbituril (CB7), catalyzes aliphatic and aromatic epoxides to give β-alkoxy alcohols under mild conditions. These molecules are important intermediates for the synthesis of many compounds such as bioactive pharmaceuticals. The unique feature of cucurbituril in the solid phase is the presence of numerous cavities in it, which has led to its enhanced capability [10].



(G) The role of ligands in catalytic water oxidation by mononuclear ruthenium complexes is well known. In this investigation, the water oxidation by ruthenium complex $[Ru(tpy)(bpg)H_2O]^{2+}$ containing a fused structure of bipyridine ligand (bpg = bipyridine glycoluril) where bpg is a multiple users ligand with 4 proton donor (N-H) and 2 proton acceptor (C=O), has been reported. According to the crystalline structure, there is an intermolecular hydrogen bonding between the (C=O) group and the bound aqua ligand [11].



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