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Green Progression for Synthesis of Regioselective β-Amino Alcohols and Chemoselective Alkylated Indoles

Boningari Thirupathi, Rapelli Srinivas, Avvari N. Prasad, J. K. Prashanth Kumar, and Benjaram M. Reddy*

Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Uppal Road, Hyderabad - 500 607, India

Abstract:

Solid acid catalysts based on zirconia materials were investigated for the first time as catalysts for regioselective organic synthesis under environmentally benign and mild conditions. The novel TiO_2-ZrO_2 mixed oxide catalyst led to two distinct products by the formation of an N−C bond (β-amino alcohols) and a C−C bond (Friedel−Crafts alkylation).

1. Introduction

Green chemistry is an important challenge in the battle to produce biologically active compounds and to replace current organic chemical processes with more environmentally benign alternatives. It is also an important task from an ecological point of view.[1] A great deal of interest has been devoted to the use of aqueous media in organic transformations because water is nontoxic, nonflammable, inexpensive, and environmentally benign.[2] Other benefits from the use of water as a medium include replacement of environmentally unfriendly, potentially dangerous, and expensive organic solvents, thereby reducing the volatile organic compounds (VOCs) released into the atmosphere.

β-Amino alcohols are known for their biological activity. They find numerous applications as amino alcohol antibiotics (**1**, Figure 1) and antibacterial drugs, which function by specifically binding to prokaryotic 16S rRNA, causing mistranslation and premature termination of mRNA translation. The targeted binding site for aminoglycosides is the A-site decoding region of prokaryotic 16S rRNA.[3] Amino alcohol or amino steroid motifs could be easily obtained through the ring-opening of the epoxides by amines. β-Amino alcohol steroids (**2**, Figure 1) serve as the basis for a wide range of biologically active natural and synthetic products.[4] A series of 2β-morpholinyl steroids have been shown to exhibit anaesthetic activity, and some have been selected for development as potential water-soluble steroidal intravenous anaesthetics.[5] Recently, a steroid possessing a methylpiperazine nucleus was reported to inhibit the proliferation of HL-60 or WEHI-3B cell lines and is a promising potential new drug for the treatment of leukemia.[6] The significant biological properties of A-ring amino moiety have urged medicinal chemists to synthesize and test a great number of novel molecules. Therefore, insertion of the amino moiety into new positions of a steroid skeleton is an important synthetic strategy in drug discovery.

Amino propanols constitute one of the most common central units of various protease inhibitors such as β- or γ-secretase,[7] HIV protease,[8] cathepsins,[9] or plasmepsins.[10] The scaffold (**3**, Figure 1) is a typical example of the 1,3-diaminoalkan-2-ol-based structure of inhibitors.[11] An intermediate in the preparation of β-secretase (**4**, Figure 1) is used in applications such as the treatment of Alzheimer's disease and as peptidomimetic inhibitors of human β-secretase.[12] A notable β-amino alcohol is propranolol (**5**, Figure 1), one of the first nonselective β-blockers developed, used extensively in the treatment of hypertension (**6**, Figure 1) and as an intermediate in the synthesis of an antitubercular drug,[13] which can be obtained by the reaction of a chlorohydrin with a nucleophile in the presence of stoichiometric amounts of a base or by the ring-opening of an epoxide,

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* Corresponding author. Telephone: +91-40-27191714. Fax: +91-40-27160921. E-mail: bmreddy@iict.res.in; mreddyb@yahoo.com.

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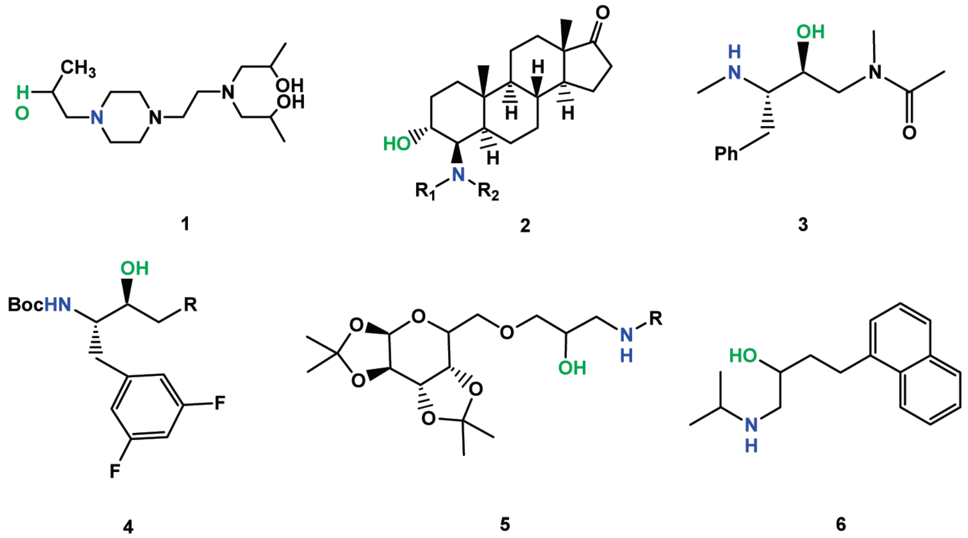

Figure 1. **Biologically active *β*-amino alcohols useful for the treatment of different diseases.**

Table 1. **Screening of various solid acid catalysts for the synthesis of *β*-amino alcohols**[a]

entry	catalyst	time (min)	yield %[b]
1	WO_x/ZrO_2	180	82
2	MoO_x/ZrO_2	180	54
3	TiO_2-ZrO_2	50	91
4	WO_x/TiO_2-ZrO_2	150	60
5	MoO_x/TiO_2-ZrO_2	150	44
6	WO_x/CeO_2-ZrO_2	180	56
7	MoO_x/CeO_2-ZrO_2	180	38
8	–	12[c]	17[d]

[a] Reagents and reaction conditions: cyclohexene oxide (1 mmol), aniline (1.2 mmol), catalyst (50 mg); unless otherwise mentioned, stirred at room temperature for an appropriate time. [b] Yields of isolated pure regeoisomers. [c] Time in hours. [d] Side products are also observed.

Table 2. **Search for optimal solvents and green conditions**[a]

entry	catalyst	solvent	time (min)	yield %[b]
1	TiO_2-ZrO_2	DCM	240	68
2	TiO_2-ZrO_2	THF	120	76
3	TiO_2-ZrO_2	ACN	120	61
4	TiO_2-ZrO_2	toluene	120	55
5	TiO_2-ZrO_2	–	50	89
6	TiO_2-ZrO_2	H_2O	50	91

[a] Reagents and reaction conditions: cyclohexene oxide (1 mmol), aniline (1.2 mmol), TiO_2-ZrO_2 (50 mg), solvent (2 mL), unless otherwise mentioned, stirred at room temperature for an appropriate time. [b] Yields of isolated pure regeoisomers.

where the epoxide is heated in the presence of the nucleophile.[14] We herein report the synthesis of *β*-amino alcohols using mild and environmentally friendly conditions. An obvious advantage of using an epoxide as a substrate in the production of *β*-amino alcohols is the general atom efficiency of the reaction.

Ecological and economic considerations have recently raised a strong interest in redesigning commercially important processes so that the use of harmful substances and the generation of toxic wastes could be avoided.[15] In this respect, heterogeneous catalytic processes are more favorable over their homogeneous counterparts in the production of fine chemicals and biological active molecules, owing to their ease of handling, simple workup procedures, and most importantly, their reusability and catalytic activity in water (green solvent). Heterogeneous mixed oxide-based solid acid catalysts such as TiO_2-ZrO_2, supported or not, have been widely used in organic syntheses. We have reported recently the oxydehydrogenation of ethylbenzene to styrene over TiO_2-ZrO_2 mixed oxide catalysts, supported or not.[16]

2. Results and Discussion

It is a gigantic challenge to treat water-insoluble organic materials in water as well as to treat water-unstable materials in water.[17] In order to find out the best catalytic system suited to the synthesis of *β*-amino alcohols, we screened typical reaction parameters including catalysts and solvents, using cyclohexene oxide (1.0 equiv) and aniline (1.2 equiv) as model substrates, and the results are summarized in Table 1 and Table 2. The preliminary exploration was carried out for the selection of a catalyst for the above reaction in solvent-free conditions. We have systematically investigated the influence of solid acids and a series of zirconia-based catalysts, metal oxides, and mixed oxides and compared them as catalysts for this reaction (Table 1). Among various catalysts we have screened, the TiO_2-ZrO_2 mixed oxide catalyst exhibited better activity and enriched regioselectivity towards desired products in these reactions. Other catalysts, namely, WO_x/ZrO_2, WO_x/TiO_2-ZrO_2, and WO_x/CeO_2-ZrO_2, also showed good activity, but the consumption of time was longer to get the desired products, and also the yields of the products were less than that of TiO_2-ZrO_2 mixed oxide.

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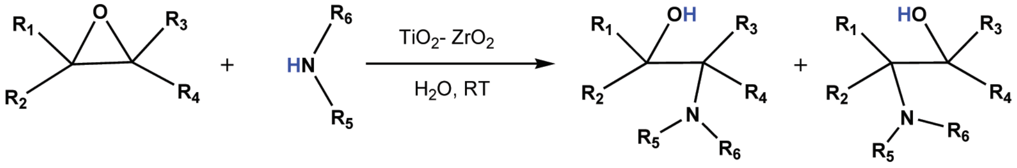
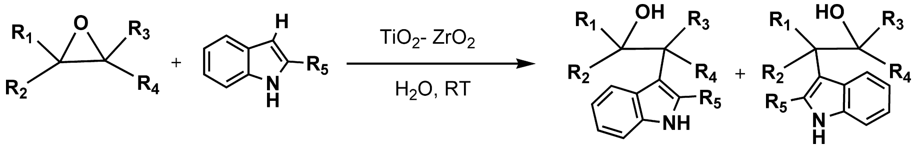
Scheme 1. Synthesis of β-amino alcohols catalysed by TiO_2-ZrO_2 mixed oxide in water



Scheme 2. Friedel-Crafts alkylation of nitrogen heterocycles with epoxides



Use of mixed oxides such as TiO_2-ZrO_2 in place of ZrO_2 is very interesting. Mixed oxides exhibit relatively high BET surface area, high thermal stability, and high mechanical strength.[18] The TiO_2-ZrO_2 mixed oxide has also been reported to exhibit high surface acidity by a charge imbalance based on the generation of Ti−O−Zr bonding.[19] The $ZrTiO_4$ compound formation was discovered while studying phase equilibria in ZrO_2 and TiO_2 systems. The $ZrTiO_4$ belongs to the space group *Pbcn* and has an orthorhombic structure (α-PbO_2) with complete disorder of the Zr^{4+} and Ti^{4+} ions on the metal sites.[20] The crystal structure consists of an edge-shared metal−oxygen octahedral [MO_6], which is quite distorted.

After selection of the most efficient catalyst, we screened different solvents to adjust the reaction conditions (Table 2). Among the reactions screened, the only ones where reactions progressed without detectable formation of byproducts used water as the solvent or no solvent at all (entries 5 and 6). The increased rates and yields are probably due to the hydrophobic nature of the reagents towards water, since their repulsion from water would enhance the collisions between the organic molecules and increase their ground-state energies, leading to an increase in the rate of the reaction.[18] To be as "green" as possible we selected water as the reaction medium and ambient temperature for mildness and economy.

With these "environmentally benign" conditions in hand, in addition to our employment of solid acid catalysts for green synthesis,[19,20] we then explored the scope of this TiO_2-ZrO_2 mixed oxide-catalysed regioselective ring-opening of diverse epoxide reactions with various amines (C−N bond formation) by using water as the solvent (Scheme 1). In addition to these reactions, we also explored ring-opening of epoxides with indoles. To our surprise, we ended up with regio-enriched Friedel−Crafts alkylation (C−C bond formation) products. To evaluate the probability of Friedel−Crafts alkylation, we extended this reaction also to the synthesis of alkylated nitrogen heterocycles by Friedel−Crafts alkylation of epoxides with indoles (Scheme 2).

Both types of reactions were carried out using a wide variety of structurally diverse amines and indoles with quite a lot of epoxides to form the corresponding β-amino alcohols and Friedel−Crafts alkylated products using TiO_2-ZrO_2 mixed oxide catalyst in water. The variation in the yields of the corresponding β-amino alcohols and alkylated products formed are found to depend on the intrinsic properties of the substituted amines and indoles employed.

Electronic effects are known to influence the reaction rates and product yields. In the case of the present reactions investigated, it is observed that the amines and indoles bearing electron-donating groups afforded the corresponding products in good yields (Table 3, entries 7, 9, 12, 14, and 18). Conversely, electron-withdrawing groups being present on the nucleophile moiety drastically decreased the rate of the reaction, and the yields of the products formed are also very low, even after extended reaction times (Table 3, entries 4 and 11).

Cyclohexene oxide with a variety of amines (Scheme 3) afforded diastereo-enriched *trans*-regioisomers (Table 3, entries 10−14) and the resultant racemic 2-amino cyclohexanol products were recognized as the *trans*-diastereoisomers on the basis of NMR spectral data. Reaction of aliphatic oxirane (propylene oxide, epichlorohydrin) with various amines and indoles afforded the major secondary alcohol regioisomer (Table 3, entries 6−9 and 15−17) by nucleophilic attack at a less sterically hindered carbon, whereas in the case of styrene oxide electronic factors predominate over the steric factors to produce a major primary alcohol regioisomer by nucleophilic attack at the more stable benzylic carbon (Table 3, entries 1−5, 18, and 19), and also the reaction is regio-enriched. In aryl oxirane, the positive charge on oxygen appears to be localized on the highly substituted benzylic carbon leading to the major product (Scheme 4). We strongly believe that rendering of the nucleophile is governed by the group environment of the oxirane and the stability of the carbonium ion.

Rationale to exhibit better catalytic activity of the TiO_2-ZrO_2 mixed oxide for the above reactions could be due to the activation of epoxide by adsorption on the surface Lewis acidic site, which is electron deficient in TiO_2-ZrO_2 mixed oxide. Epoxides are able to act as Lewis bases directly through their nonbonded electron pairs, confirming that the presence of Lewis acids in these reactions enhances the rate of ring-opening processes, primarily by weakening the already strained C−O bond. On the other hand, the surface Lewis basic site, which is created by surface $Ti-O^-$, is specific for the generation of a nucleophile by proton abstraction from amines or indoles. This suggests that the surface Lewis acidic site is responsible for

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Table 3. **Amination of epoxides and alkylation of indoles over TiO_2-ZrO_2 in water**[e]

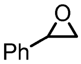
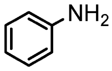
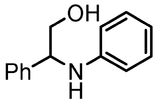
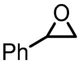
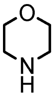
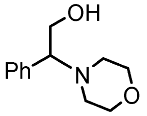
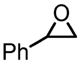
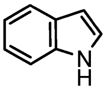
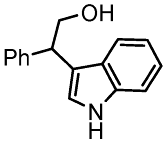
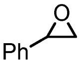
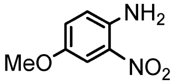
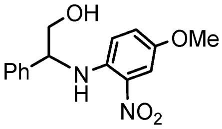
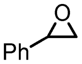
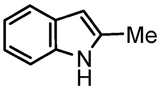
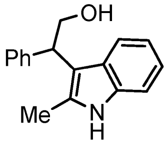
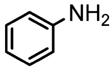
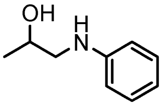
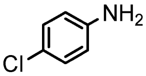
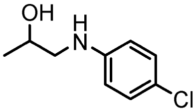
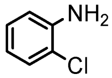
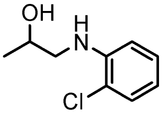
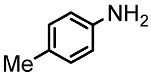
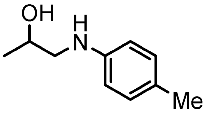
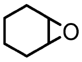
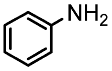
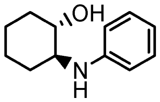
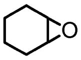
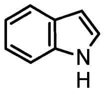
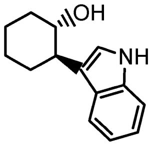
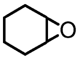
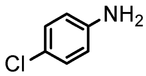
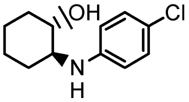
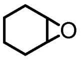
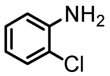
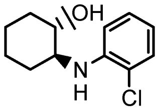
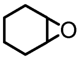
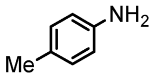
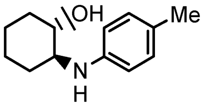
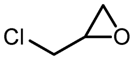
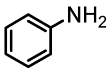
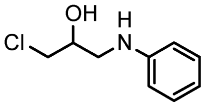
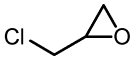
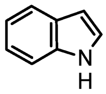
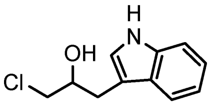
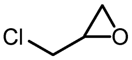
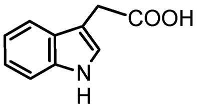
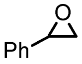
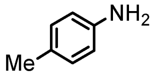
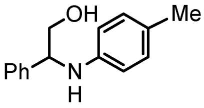
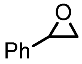
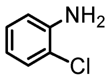
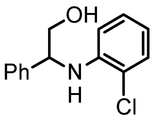
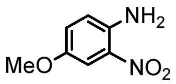
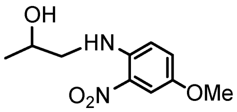
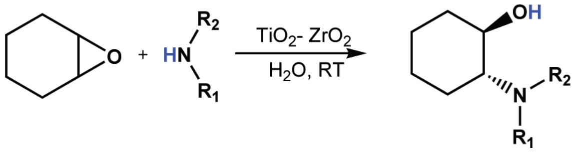
Entry	Epoxide	Amine	Major regioisomer	Ratio (A:B)[a]	Time (min.)	Yield (%)[b]
1.				92:08	80	86
2.				~100:00	50	75
3.				91:09	60	78
4.				89:11	90	82
5.				94:06	45	84
6.				94:06	210	79
7.				96:04	240	88
8.				91:09	180	75
9.				97:03	210	96
10.				~100:00	50	91
11.				—	12[c]	traces
12.				~100:00	150	93

Table 3. **Continued**

Entry	Epoxide	Amine	Major regioisomer	Ratio (A:B)[a]	Time (min.)	Yield (%)[b]
13.				~100:00	180	74
14.				~100:00	150	94
15.				88:12	95	92
16.				~100:00	70	86
17.			—	—	12^{c}	—[d]
18.				92:08	60	88
19.				85:15	60	87
20.				98:02	130	45

[a] Yields of isolated pure regeoisomers A:B. [b] Isolated yield of the products. [c] Time in days. [d] Starting materials are recovered. [e] Reagents and reaction conditions: epoxide **1** (1 mmol), **2** amine/indole (1.2 mmol), TiO_2-ZrO_2 (50 mg), water (2 mL) stirred at room temperature for an appropriate time.

Scheme 3. **Highly regio-enriched ring-opening of symmetrical epoxide**

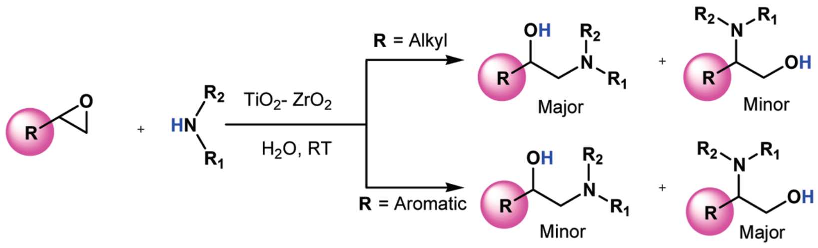


the activation of epoxide, and the Lewis basic site is responsible for the generation of a nucleophile (Figure 2).

3. Conclusions

In conclusion, we have reported *for the first time* an original use of TiO_2-ZrO_2 mixed oxide as catalyst for regioselective organic synthesis in water. With such a

Scheme 4. **Desired product differentiations by changing the nature of unsymmetrical epoxide**



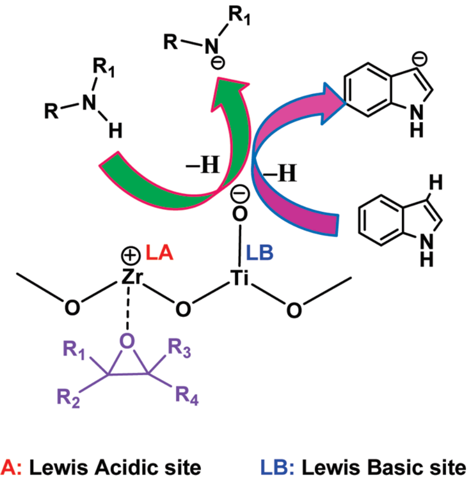


Figure 2. **Exact catalyst surface sites for the activation of epoxide and generation of nucleophile.**

catalyst, we have developed a simple and efficient method for the regio-enriched ring-opening of epoxides (C−N bond construction) and chemoselective Friedel−Crafts alkylation of indoles with epoxides (C−C bond construction). Moreover, the same TiO_2-ZrO_2 mixed oxide catalyst has been used for both reactions (see Figure 3). These results thus broaden the scope of the so-called synthesis of β-amino alcohols and Friedel−Crafts alkylation.

4. Experimental Section

4.1. Catalyst Preparation. TiO_2-ZrO_2 (1:1 mol ratio based on oxides) mixed oxide was prepared by adopting a coprecipitation method by hydrolysis with dilute aqueous ammonia solution. For this purpose, the requisite quantity of $ZrOCl_2 \cdot 8H_2O$ (Loba Chime, GR grade) and $TiCl_4$ (Fluka, AR grade) were dissolved separately in double distilled water and mixed together. Cold titanium(IV) chloride was digested first in cold concentrated HCl and diluted with deionized water. To the solution mixture was added dropwise aqueous NH_3 with vigorous stirring until the pH of the solution reached 8.The resulting precipitate was allowed to settle down for 2 days. The obtained precipitate was then filtered off, washed several times with deionized water and hot distilled water until free from (chloride) anion impurities, and oven-dried at 393 K for 12 h. A portion of the oven-dried material was calcined at 923 K for 5 h in air atmosphere. The prepared catalyst was characterized by various physicochemical techniques, namely, X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, and other methods. The characteristic features of the synthesized TiO_2-ZrO_2 mixed oxide catalyst are included in the Supporting Information.

4.2. Typical Experimental Procedure and Reusability. All chemicals employed in this study were commercially available and used without further purification. A mixture of epoxide (1 mmol), amine or indole (1.2 mmol), and TiO_2-ZrO_2 mixed oxide catalyst (50 mg) in water (2 mL) was stirred at room temperature for an appropriate time. After completion of the reaction, as indicated by TLC, the reaction mixture was filtered and washed with ethyl acetate (3 × 5 mL), and the combined layers were dried over anhydrous Na_2SO_4, concentrated in vacuum, and purified by column chromatography on silica gel using ethyl acetate and hexane as an eluent to afford pure β-amino alcohols and Friedel−Crafts alkylated

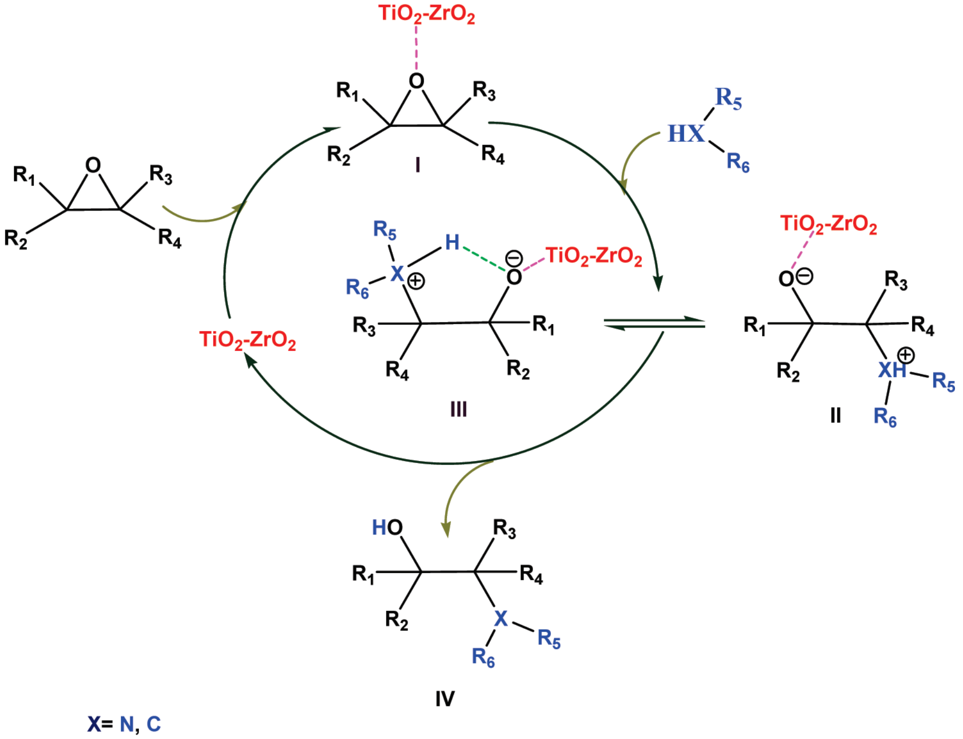


Figure 3. **Plausible reaction mechanism for both syntheses catalysed by TiO_2-ZrO_2.**

indoles. All products were identified by comparing their spectral data with literature.[21−25]

The solid catalyst was conveniently removed by simple filtration from the reaction mixture. The wet catalyst was reused for the reaction, and there was no big change in the catalytic activity in the next five cycles.

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Supporting Information Available

^{1}H NMR, FTIR, and MS data of all isolated products, and X-ray powder diffraction, Raman, and XPS analysis of the catalyst. This material is available free of charge via the Internet at http://pubs.acs.org/.

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