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MINI REVIEW

A Brief Study on the Role of Silicotungstic Acid in Modern Organic Syntheses

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This review article aimed to discuss the remarkable role of silicotungstic acid as an efficient catalyst in a variety of organic reactions like synthesis of natural products or biologically potent organic scaffolds or its precursors which have wide ranging pharmaceutical and industrial implementations. These reactions were carried out either in presence of solvent or under solvent-free condition. Moreover, miscellaneous solid surfaces supported silicotungstic acid had a wide array of potential applications. The present study compiled some of these assorted reactions and makes a contrast of different kinds of reactions.

Keywords: Heteropoly acids, Silicotungstic acid, Heterogeneous catalyst, Supported STA.

INTRODUCTION

In the last three decades, solid heteropoly acids (HPAs) have emerged as useful and versatile catalyst for some acid catalyzed organic reactions [1,2]. Heteropoly acids (HPAs) are usually solids that are highly soluble in polar solvents. They can be used as in bulk or supported forms in both homogenous and heterogeneous systems [3-6]. There are already several large scale industrial processes using HPA catalysts [7,8]. Additionally, HPAs have several merits, including high flexibility on modification of the acid strength, ease of handling, environmental compatibility, non-toxicity and experimental simplicity [9]. In recent years, the implementation of solid acids as a heterogeneous catalyst has received considerable interest in various fields of organic synthesis [10-14]. Heteropoly acids (HPAs) were found to exhibit excellent catalytic activities in the dehydration of diols [15], rearrangements [16], tetrahydropyranylation of alcohols [17], Friedel-Craft alkylation [18], Prins reaction [19], pyrimidine synthesis [20], Biginelli reaction [21], Dakin-West reaction [22] and acetylation reaction [23]. Moreover, modified HPAs have received increasing attention over the last few years as solid high-proton conductors owing to their applications in the field of fuel cells, sensors, electrochemical chromogenic devices, *etc*. [24,25].

There is a prodigious structural diversity of heteropoly acids (HPAs) concerning the structure of heteropolyanion (Table-1) [26].

TABLE-1
MAIN HETEROPOLYANIONS AND
THEIR CHEMICAL FORMULAE [Ref. 26]

Series	Heteropolyanions	Central unit
Keggin	$X^{n+}M_{12}O_{40}^{(8-n)-}$	XO_4
Dawson	$X^{2n+}M_{18}O_{62}^{(16-2n)-}$	XO_4
Anderson	$X^{n+}M_6O_{24}^{(12-n)-}$	XO_6
Waugh	$X^{n+}M_9O_{32}^{(10-n)-}$	XO_6
Silverton	$X^{n+}M_{12}O_{42}^{(12-n)-}$	XO_4

Among the HPAs, the compounds of Keggin structure are known for their good thermal stability, high acidity and high oxidizing capability and are used for various organic transformations. The Keggin type HPAs have the formula $H_{8-n}XM_{12}O_{40}$, where X is the central atom (Si^{4+}, P^{5+}, *etc*.), n is the oxidation state of X and M is the metal ion (W^{6+} or Mo^{6+}). Solid heteropoly acids (HPAs) have discrete ionic structures that contain heteropolyanion (polyoxometalate) units and countercations [1,27,28].

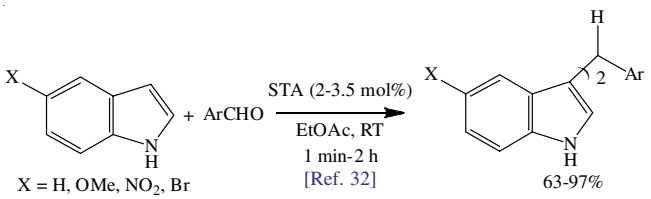
In recent years, HPAs explicitly, phosphomolybdic acid, phosphotungstic acid and silicotungstic acid (STA) have been put into operation for a variety of synthetic purposes. Their

significant higher Brønsted acidity as compared with that of other traditional solid acids has augmented their significance in catalytic applications [29]. Silicotungstic acid, $H_4SiW_{12}O_{40}$ is one of the promising Keggin types of HPAs because it has high catalytic activity, good stability, economically attractive and environmentally benign. In year 1863, Marignac [30] first claimed to have prepared STA. Later in 1925, North and Beal [31] enlarged the usefulness of this reagent by producing it in the form of a dry powder, stable in air and readily handled without decomposition.

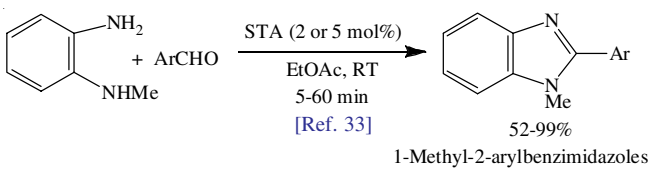
The present article is intended to review briefly the literature published from the year 2000 onwards. However, for the purpose of aiding the meticulous discussion, some former studies were also included. All these references mainly focused on the advancement of STA as a catalyst in homogeneous and heterogeneous systems and some representative works are precisely discussed below:

Solution phase organic reactions catalyzed by silicotungstic acid (STA)

Synthesis of some pertinent nitrogen heterocycles: A brief discussion of certain homogeneously catalyzed organic reactions is presented in this category. In the early 21st century, Chakrabarty *et al*. [32] have designed an efficient protocol for the solution-phase synthesis of nitrogen heterocycles like symmetrical bisindolylalkanes (using substituted indoles and aryl aldehydes) (**Scheme-I**) and 1-methyl-2-arylbenzimidazoles [33] (using substituted *N*-methyl *o*-phenylene diamines and aryl aldehydes) (**Scheme-II**) using homogeneous catalyst STA. The reactions were carried out in ethyl acetate solvent at room temperature. The indoles and imidazoles, both substituted and annulated, are present in many natural and synthetic products possessing a wide range of pharmacological activities. Both these class of compounds displayed significant anticancer, antiviral, antiallergic, antiulcer and anticoagulant properties in human therapeutics [34-42].

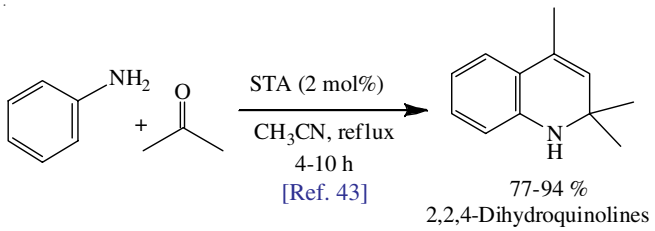


Scheme-I: Synthesis of symmetrical bisindolyl alkanes



Scheme-II: Synthesis of 1-methyl-2-arylbenzimidazoles

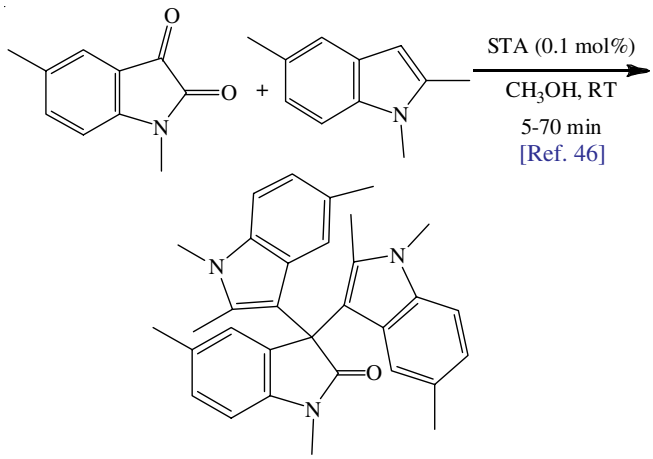
Kamakshi and Reddy [43] achieved the STA catalyzed synthesis of several 2,2,4-dihydroquinolines in good yields from substituted anilines, acetone or methyl ethyl ketone in acetonitrile solvent (**Scheme-III**). Dihydroquinoline moiety



Scheme-III: Synthesis of 2,2,4-dihydroquinolines

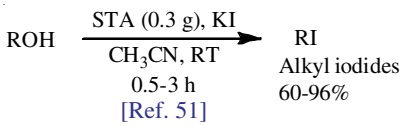
occupies an essential place in the realm of natural products and it had attracted a lot of attention from synthetic organic chemists [44]. It forms the parent bicyclic system for an extensive array of medicinally interesting compounds. Substituted dihydroquinolines have been used to produce potent drugs with bactericidal, antimalarial and anti-inflammatory properties [45].

Recently, Nikoofar [46] discussed about the condensation of various isatins with heteroaromatics (indoles and pyrrole) in the presence of STA catalyst at room temperature to form their corresponding pharmacologically valuable 3,3-*bis*(indolyl)- and 3,3-*bis*(2-pyrrolyl)oxindoles [47-49] efficiently (**Scheme-IV**) using methanol as solvent, which is environmentally benign.



Scheme-IV: Synthesis of 3,3-*bis*(indolyl)oxindoles

Synthesis of alkyl iodides: The direct conversion of alcohols to alkyl iodides is a transformation which is widely utilized in organic synthesis [50]. In 2011, STA was used as an effective catalyst for the conversion of a wide range of allylic, secondary aliphatic and benzylic alcohols to the corresponding iodides in acetonitrile solvent at room temperature (**Scheme-V**) [51]. Excellent yield, short reaction time, simple work up procedure and efficient recovery were the key features of these synthetic methodologies.



Scheme-V: Preparation of alkyl iodides

Silicotungstic acid (STA) catalyzed organic reactions under green solvent-free environment

Some distinctive one-pot multicomponent reactions for the synthesis of annulated aromatic compounds: With the increasing public concern over environmental degradation, the application of solvent-free reactions and user-friendly catalyst represents a powerful green chemical technology from both the economic and synthetic point of view.

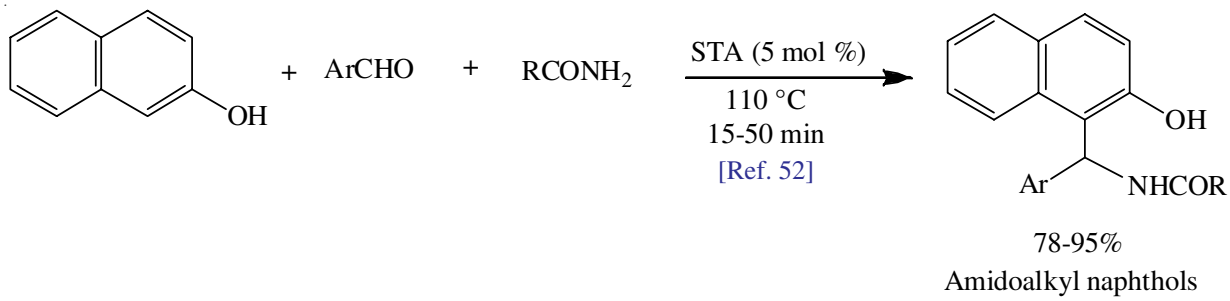
Supal and Gokavi [52] studied about a solvent-free zipper reaction, where the synthesis of amidoalkyl naphthols was carried out by the condensation of aromatic aldehydes, 2-naphthol and substituted amide using STA as an eco-friendly catalyst (**Scheme-VI**). 1-Amidoalkyl-2-naphthols are important intermediates, which can be easily converted into biologically active 1-amino-alkyl-2-naphthols derivatives by amide hydrolysis. The hypertensive and bradycardiac effects of these compounds have been evaluated [53,54].

Bandgar *et al.* [55] developed a series of pyranopyrazoles, which was methodologically synthesized *via* one-pot, four component reaction of ethyl acetoacetate, hydrazine hydrate, aldehydes and malononitrile in presence of catalytic amount of STA (**Scheme-VII**). Pyranopyrazoles are reported to possess a multiplicity of pharmacological properties including anticancer, antimicrobial, anti-inflammatory, insecticidal and molluscicidal activities [56-60]. They also found applications as pharmaceutical ingredients and biodegradable agrochemicals [61-64].

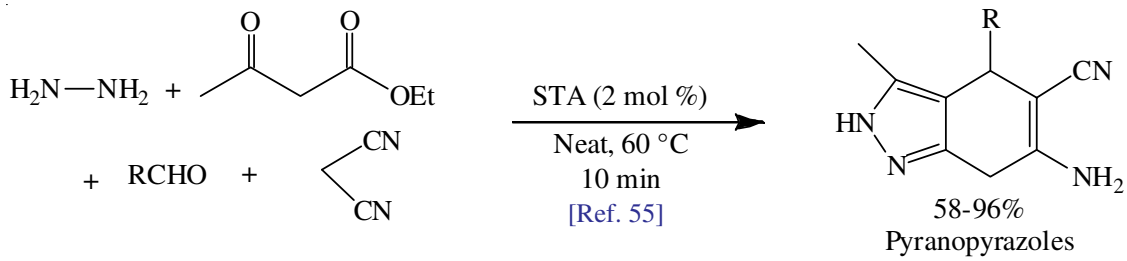
Recently, Chavan *et al.* [65] have described magnificently a sequential synthesis of 12-aryl/alkyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones under solvent free condition by the condensation of 2-naphthol, aldehydes and dimedone (**Scheme-VIII**). Xanthenes and benzoxanthenes are important biologically active heterocycles possessing antiinflammatory, antiviral and antibacterial activities [66-68].

Some more examples of eco-friendly solvent-free reactions catalyzed by STA

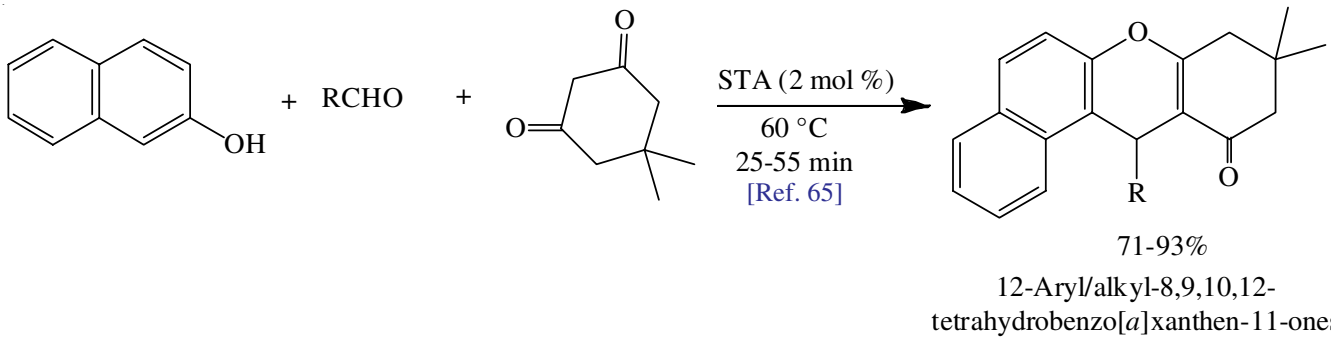
Organic reactions without the use of harmful organic solvents are one of the current focuses of environmentally conscious society. Hence, STA was used as catalyst for a wide array of organic reactions under solvent-free condition. These reactions were (i) Quantitative oxidation of cyclohexene to adipic acid [69] under ultrasound irradiation at room temperature (**Scheme-IX**); (ii) Mannich reaction, where 1,5-benzodiazepines were synthesized by condensation of *ortho*-phenylenediamine with



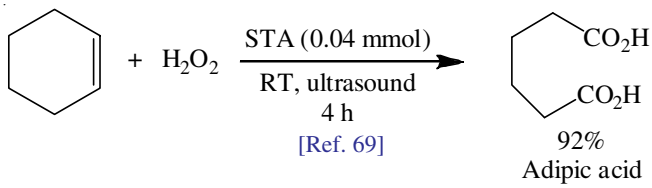
Scheme-VI: Synthesis of amidoalkyl naphthols



Scheme-VII: Synthesis of pyranopyrazoles

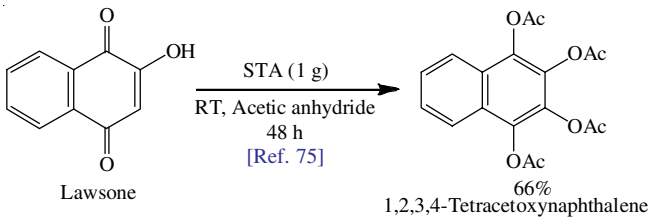


Scheme-VIII: Synthesis of 12-aryl/alkyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-ones



Scheme-IX: Synthesis of adipic acid

ketones [70]. Benzodiazepines are important pharmaceutical compounds that were frequently used as prescribed drugs for combating central nervous system related diseases mainly because of their anticonvulsant, hypnotic and other properties [71,72]. In the same study, β-amino carbonyl compounds (important building block for construction of various nitrogen containing natural products and pharmaceutical) [73,74] were also synthesized *via* reaction of aromatic ketones, aromatic aldehydes and aromatic amines under solvent free conditions in good to excellent yields (**Scheme-X**); and (iii) acetoxylation reaction [75], where 1,2,3,4-tetracetoxynaphthalene (precursor of natural antibiotic) [76,77] was synthesized successfully from lawsone at room temperature (**Scheme-XI**).



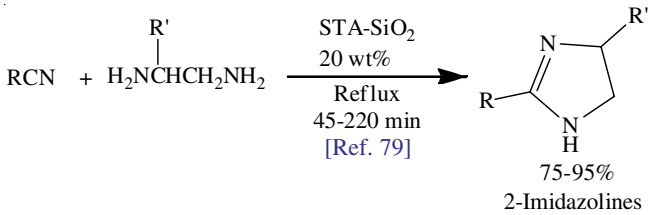
Scheme-XI: Synthesis of 1,2,3,4-tetracetoxynaphthalene

The mild reaction conditions, short reaction periods, reasonable yields of the products and easily available, inexpensive and eco-friendly catalyst (STA) render the above-mentioned reaction methodologies attractive in comparison to their extend synthetic routes.

Green organic reactions catalyzed by solid surfaces supported silicotungstic acid (STA): The development of an efficient and a non-hazardous catalyst, which is easy to handle, is highly challenging in any organic syntheses. Some of these problems can be overcome by employing heterogeneous solid catalysts, which have several intrinsic advantages like the ease of product separation, recyclability of catalyst and the minimization of waste production. In recent years, a vast domain of eco-compatible reactions was reported under this category. The solids supported STA catalysts can be easily separated and reused in solvent-free strategy without loss of its efficiency.

Typical models of solid surfaces supported STA

(A) Silica supported STA: This methodology is generally used in (i) Friedel-Crafts alkylation and acylation reaction [78]; (ii) multicomponent reaction [79] for the synthesis of imidazolines and bisimidazolines (**Scheme-XII**) (imidazoline derivatives are of great interest and importance because of their pharmaceutical and synthetic material applications) [80-83]; (iii) acetylation of alcohols and phenols [84]; and (iv) synthesis of diacetals from aldehydes and ketones (**Scheme-XIII**) [85];



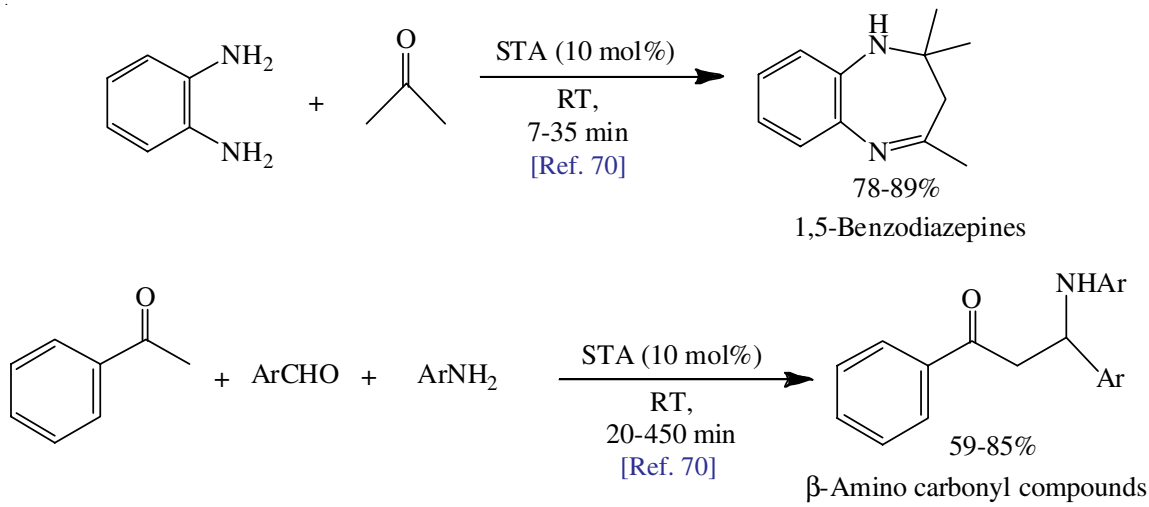
Scheme-XII: Synthesis of 2-imidazolines (Multicomponent reaction)

(B) STA encapsulated on UiO-66: The catalyst (UiO-66 is a metal organic framework made of $Zr_6O_4(OH)_4$ with 1,4-benzodicarboxylic acid) had a promising role in esterification of lauric acid with methanol to produce biodiesel (**Scheme-XIV**) [86].

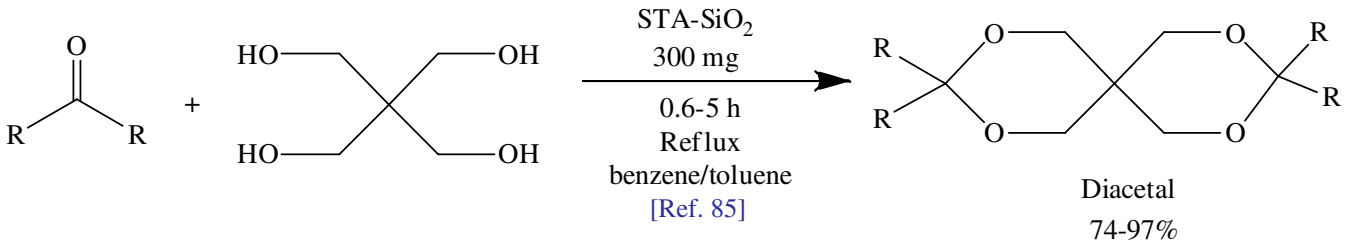
(C) STA-bentonite clay catalyst: In the synthesis of acetals and ketals (**Scheme-XV**) [87].

(D) STA-Amberlyst 15 resin catalyst: This type of catalyst is generally used in Aza-Friedel-Crafts reaction (**Scheme-XVI**) [88].

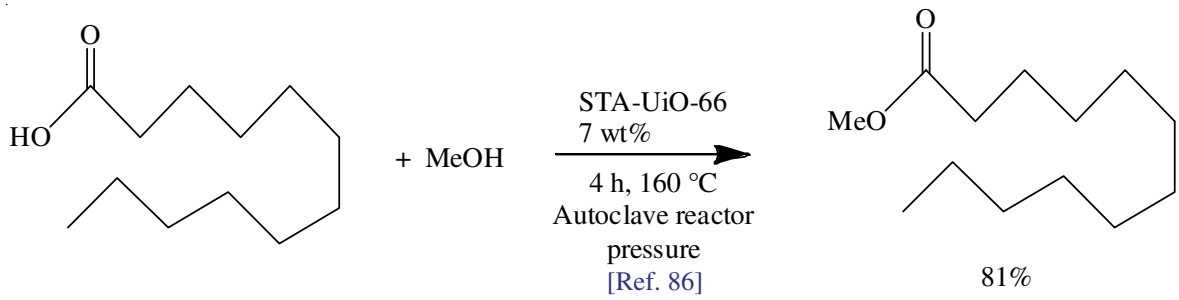
(E) Substituted metal and/or doped STA: (i) Silver salt of STA catalyst used in the synthesis of biologically profound benzodiazepines (**Scheme-XVII**) [89]; (ii) tin salt of STA doped on silica for the synthesis of various benzoxazoles [90].



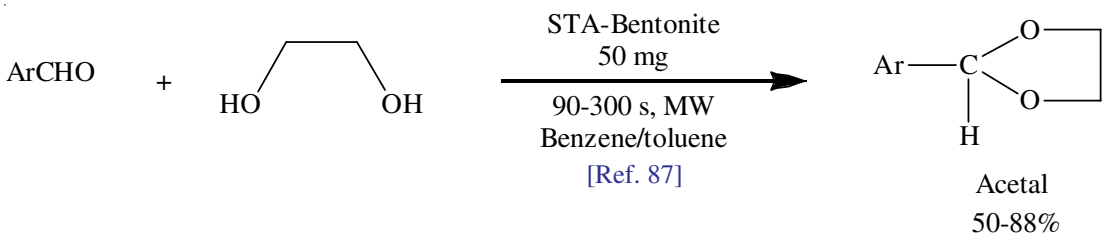
Scheme-X: Synthesis of 1,5-benzodiazepines and β-amino carbonyl compounds



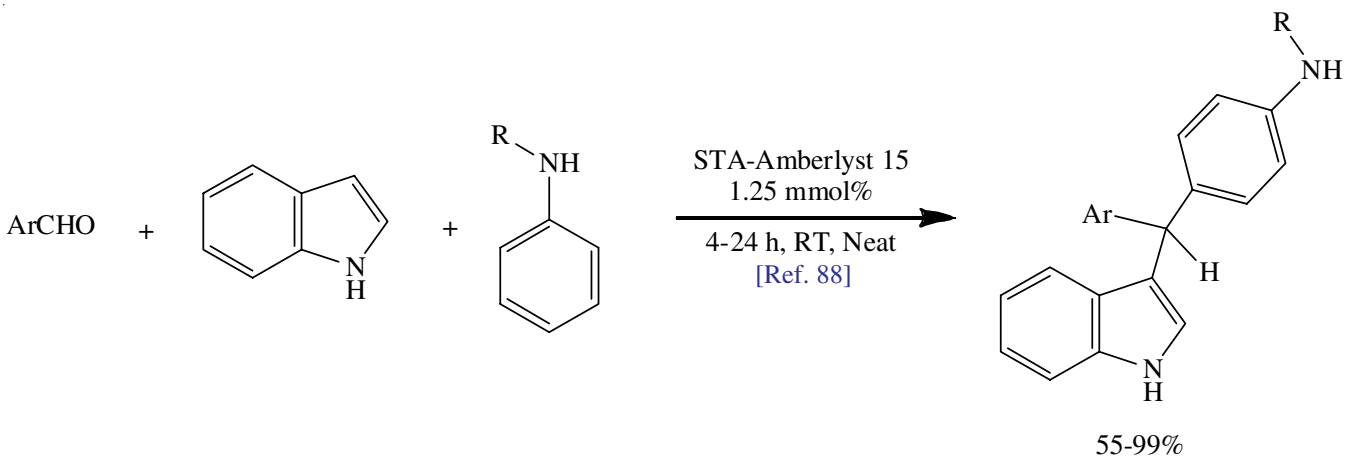
Scheme-XIII: Synthesis of diacetals from aldehydes and ketones



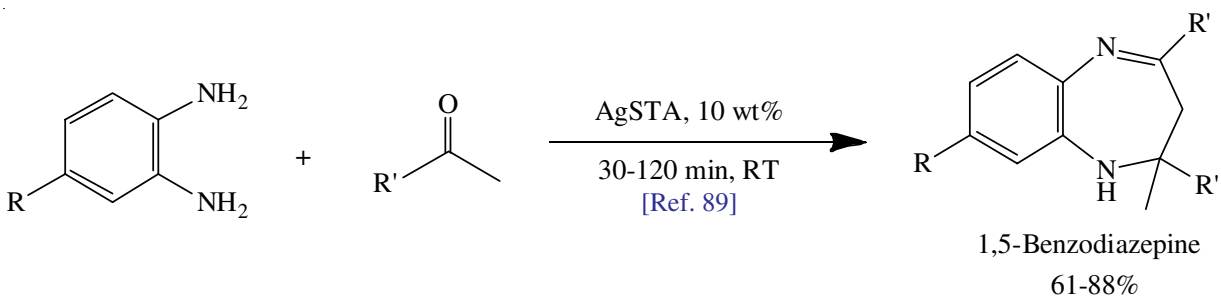
Scheme-XIV: Esterification of lauric acid with methanol



Scheme-XV: Preparation of acetals and ketals



Scheme-XVI: Aza-Friedel-Crafts reaction



Scheme-XVII: Synthesis of 1,5-benzodiazepine

Miscellaneous examples of solid surfaces doped STA: Heterogeneous inorganic techniques had become a valuable tool for solvent-free synthetic routes and received tremendous attention in modern organic chemistry. Some of the examples are (i) MCM-41 (a mesoporous material with a hierarchical structure from a family of silicate and alumosilicate) supported STA was used as an effective catalyst in the esterification reaction of lauric acid with glycerol [91] and in the esterification of dicarboxylic acids with butanol [92]; (ii) SBA-15 (a mesoporous silica sieve) supported STA in presence of phase-transfer catalyst (PTC) for carrying out epoxidation reaction [93]; (iii) zirconia-STA for the production of a versatile intermediate acrolein in chemical industries [94] and biologically potent imidazoles [95]; (iv) Pt-alumina mixture doped STA for the synthesis of 1,3-propanediol, a precursor of polyester [96]; (v) γ-alumina-STA for the synthesis of α-aminonitrile [97], *etc*.

A composite membrane was prepared from sulfonated polyarylene ether sulfone embedded with powdered STA [98]. Recently, Matsuda *et al*. [99] designed one inorganic-organic composite membrane by using partly cesium-substituted STA doped with polybenzimidazole. These doped STAs found extensive application as medium temperature polymer electrolyte fuel cells due to good proton conductivity, excellent thermal stability and mechanical strength. Moreover, STA doped phosphoric acid imbibed polybenzimidazole was reported to be used as high temperature proton exchange membrane fuel cell owing to enhanced protonic conductivity and strong mechanical stability [100].

Conclusion

Silicotungstic acid (STA) in altered form are gaining prominence due to the development and commercialization of several industrial processes based on STA catalysis. The catalyst is advantageous due to its inexpensiveness, eco-friendliness and nil production of toxic chemicals. The current review provides an overview of the assembled literature that would help to understand the role of STA in diverse system and also generalizes STA as a beneficial catalyst in the synthesis of novel organic compounds, which brings great advancement in modern chemistry.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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