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Silica Tungstic Acid and Sulphated Silica Tungstic Acid as Highly Efficient Solid Acid Catalysts for the Synthesis of Pyrrole Derivatives[1]

F. Moradgholi*, J. Lari, and Y. Baratian

Chemistry Department, Payame Noor University, Tehran, 19395-4697 Iran
**e-mail: fateme.moradgholi@gmail.com*

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Abstract—In the present study silica supported tungstic acid (STA) and sulphated silica tungstic acid (SSTA) were applied as efficient and cost-effective solid acid catalysts in the synthesis of N-substituted pyrrole derivatives via the Paal–Knorr reaction of 2,5-hexadione with aromatic and aliphatic amines at room temperature. The reaction completed in short time under mild conditions with high yield. The catalysts could be easily recovered upon reaction completion. Structures of all products were confirmed by elemental analysis, FT-IR, ^{1}H and ^{13}C NMR spectra.

Keywords: Paal–Knorr, pyrrole, sulphated silica tungstic acid, 2,5-hexadione, silica tungstic acid

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INTRODUCTION

Various methods have been worked out for synthesis of pyrroles, including the Knorr [1], Hantzsch [2] and Paal–Knorr [3, 4] reactions. Pyrrole structures were found in the molecules of some natural compounds such as chlorophyll, vitamin B12 and many others [5].

The widely used Paal–Knorr reaction was usually catalyzed by various Lewis or Brønsted acids, montmorillonite KSF-clay and iodine [6], aluminum oxide [7], ionic liquids [8], zeolites [9, 10], sulfamic acid [11], $Bi(NO_3)_3{\cdot}5H_2O$ [12], $Sc(OTf)_3$ [13], zirconium phosphate and zirconium sulfophenylphosphonate [14], Ti $(OPri)_4$ [15], Al_2O_3 [16], and *p*-TSA [16]. However, they are characterized by certain drawbacks including long reaction time, harsh reaction conditions, toxic solvents used, and complicated products separation. Some catalysts are corrosive and often cause environmental problems. Therefore, development of simple, efficient and environmentally friendly methods under the action of new catalysts for the Paal–Knorr reaction was highly desirable.

In the recent studies silica supported tungstic acid (STA) and sulphated silica tungstic acids (SSTA) catalyzed efficiently numerous organic reactions [18–20]. The clear advantages of those catalysts initiated our application of STA and SSTA as heterogeneous acid catalysts in the synthesis of *N*-substituted pyrrole derivatives.

EXPERIMENTAL

Chemicals were purchased from Merck and Fluka. IR spectra were recorded on a Shimadzu 8300 spectrophotometer. NMR spectra were measured on a BrukerAvance DPX-400 spectrometer in $CDCl_3$. Purity of products and progress of the reactions were monitored by TLC (silica-gel polygram SILG/UV254 plates). Elemental analysis was performed on a Thermo Finnigan Flash EA micro analyzer. X-ray powder diffraction studies were carried out on a Rigaku Geigerflex-3034 diffractometer in the 2θ range of 10–90 degrees using CuK_α radiation ($\lambda = 1.54$ Å).

Preparation of silica tungstic acid (STA) [18, 19]. Oven dried silica-gel 60 (10 g) was added to thionyl chloride (40 mL) in a round bottomed flask (250 mL) equipped with a condenser with a $CaCl_2$ drying tube. The mixture was refluxed upon stirring for 48 h. Silica chloride was filtered off and dried. Silica chloride **5** (6 g) and 7.03 g of sodium tungstate were added to 20 mL of *n*-hexane and the mixture was refluxed for 6 h. The reaction mixture was filtered,

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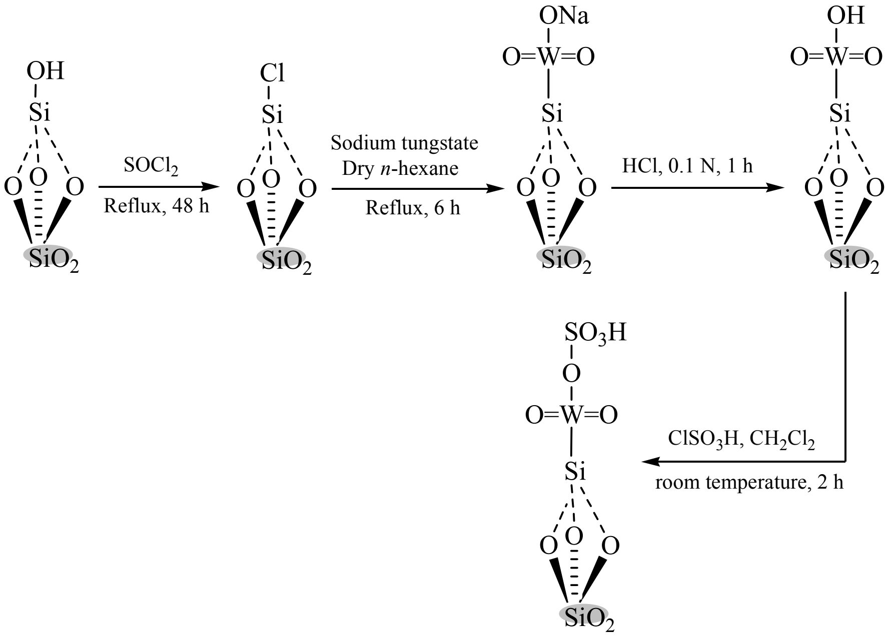
[1] The text was submitted by the authors in English.

Scheme 1. Preparation of the catalyst.



washed with distilled water and dried. The dry mixture was stirred in 0.1 N HCl (40 mL) for 1 h. STA was filtered off, washed with distilled water and dried.

Preparation of sulphated silica tungstic acid (SSTA) [20]. A suction flask was equipped with a constant pressure dropping funnel and a gas outlet tube for passing HCl gas through an adsorbing solution of a water trap. 1 mL Of cholorosulfonic acid was added dropwise to a mixture of 2.5 g STA and 75 mL dichloromethane at room temperature. Upon completion of addition, the mixture was stirred for 90 min for total elimination of HCl gas. The resulting sulphated-STA was separated and washed several times with dichloromethane and dried at 120°C for 3 h.

Synthesis of 2,5-dimethyl-1-phenyl-1*H*-pyrrole catalyzed by STA. *Method a*. 2,5-Hexadione (1.1 mmol), aniline (1 mmol) and ethanol (0.5 mL) were mixed with STA (0.1 g) and stirred at room temperature for an appropriate time. Upon completion of the reaction, as indicated by TLC (*n*-hexane–ethyl acetate = 8 : 2), ethanol was added solubilizing the product. The remaining solid catalyst was filtered off and washed with ethanol. The solvent was evaporated under reduced pressure to give the product.

Synthesis of 2,5-dimethyl-1-phenyl-1*H*-pyrrole catalyzed by SSTA. *Method b*. The synthesis was carried out the same way as described above for method *a* but catalyzed by SSTA (0.07 g).

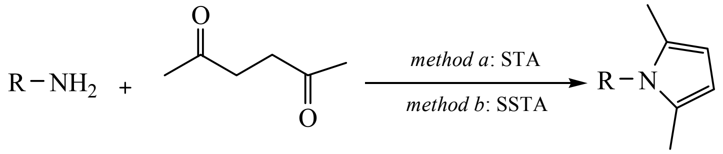
1-(4-Ethoxyphenyl)-2,5-dimethyl-1*H*-pyrrole. IR spectrum, ν, cm^{-1}: 2977 (C–H), 1515 and 1404 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.25 t (*J* = 6.8 Hz, 3H), 2.09 s (6H), 4.14 t (*J* = 6.8 Hz, 2H), 5.95 s (2H), 7.02 d (*J* = 8.8 Hz, 2H), 7.18 d (*J* = 8.8 Hz, 2H). ^{13}C NMR spectrum, δ, ppm: 13.0, 14.9, 63.71, 105.3, 114.73, 129.2, 129.3, 131.6, 158.3. Found, %: C 78.14; H 7.93; N 6.7. $C_{14}H_{17}NO$. Calculated, %: C 78.11; H 7.95; N 6.5.

4-(2,5-Dimethyl-1*H*-pyrrol-1-yl)phenol. IR spectrum, ν, cm^{-1}: 3412 (OH), 2953 (C–H), 1562 and 1458 (C=C). ^{1}H NMR spectrum, δ, ppm: 2.05 s (6H), 5.32 br (1H), 5.92 s (2H), 6.91 d (*J* = 8.8 Hz, 2H), 7.09 d (*J* = 8.8 Hz, 2H). ^{13}C NMR spectrum, δ, ppm: 12.9, 105.2, 115.8, 129.2, 129.3, 131.6, 155.3. Found, %: C 75.34; H 8.97; N 7.3. $C_{12}H_{13}O$. Calculated, %: C 75.36; H 8.95; N 7.32.

3-(2,5-Dimethyl-1*H*-pyrrol-1-yl)phenol. IR spectrum, ν, cm^{-1}: 3409 (OH), 2920 (C–H), 1600 and 1492 (C=C). ^{1}H NMR spectrum, δ, ppm: 2.07 s (6H), 5.32 br (1H), 5.93 s (2H), 6.616 t (*J* = 2 Hz, 1H), 6.78–7.09 m (2H), 7.32 d (*J* = 8 Hz, 1H). ^{13}C NMR spectrum, δ, ppm: 12.9, 105.5, 114.8, 115.3, 120.6, 129.0, 129.9, 140.1, 156.1. Found, %: C 75.37; H 8.96; N 7.31. $C_{12}H_{13}O$. Calculated, %: C 75.36; H 8.95; N 7.32.

2,5-Dimethyl-1-*p*-tolyl-phenyl-1*H*-pyrrole. IR spectrum, ν, cm^{-1}: 2982(C–H), 1523 and 1434 (C=C). ^{1}H NMR spectrum, δ, ppm: 2.07 s (6H), 2.78 s (3H), 5.92 s (2H), 6.92 d (*J* = 8.8 Hz, 2H), 7.09 d (*J* = 8.8 Hz,

Scheme 2. Synthesis of substituted pyrroles.



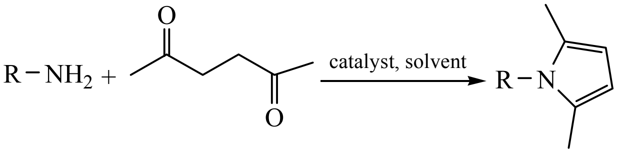
2H). Found, %: C 84.32; H 8.17; N 7.53. $C_{13}H_{15}N$. Calculated, %: C 84.28; H 8.15; N 7.56.

RESULTS AND DISCUSSION

Recently, STA and SSTA have been used as silica supported solid acids in some organic transformations [21–23] (Scheme 1).

Interaction of sulfonic groups and tungsten moieties with silica surface was studied by FT-IR spectra. FT-IR spectrum of sodium tungstate demonstrated the WO_4^{2-} stretching vibrations band at 1680 cm^{-1}, STA similar band at 1634 cm^{-1} and a band attributed to SiO_2 stretching vibrations. Introduction of the SO_3^{2-} groups in STA led to decrease in intensity of the WO_4^{2-} stretching vibrations. Bands at ca. 1200–1250, 1177, and 750–1000 cm^{-1} were attributed to the O=S=O asymmetric and symmetric stretching vibrations and S–O stretching vibrations of the sulfonic groups, respectively.

Table 1. Optimization of the reaction conditions



Solvent	*Method a*[a]			*Method b*[a]		
	STA, g	time, h	yield, %	SSTA, g	time, min	yield, %
CH_3CN	0.10	2 : 25	89	0.070	90	85
CH_2Cl_2	0.10	3	80	0.070	120	80
EtOH	0.10	2	92	0.070	75	95
Solvent-free	0.10	1 : 30	80	0.070	90	90
EtOH	0.70	3	87	0.025	120	87
EtOH	0.35	4 : 30	89	0.050	120	90
EtOH	0.60	4	91	0.100	75	94
EtOH	0.20	2	90	–	–	–

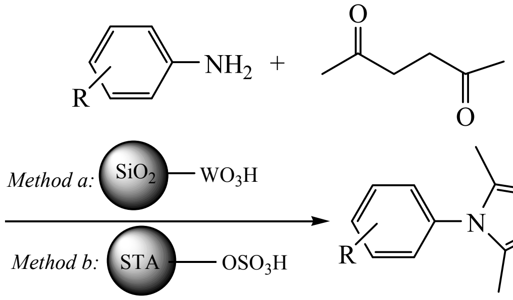
[a] Reaction conditions: amine (1 mmol), 2,5-heptadione (1.1 mmol) in room temperature, *method a*: STA and *method b*: SSTA.

XRD patterns of STA and sulphated silica tungstic acid demonstrated the presence of a broad peak around $2\theta = 22°$ that indicated the link of WO_3 to silica gel.

STA and SSTA were used in the synthesis of pyrrole derivatives by the reaction of 2,5-hexadione with aromatic amines (Scheme 2).

The reaction of aniline (1 mmol) with 2,5-hexadione (1.1 mmol) was used as the model for the process optimization (Table 1). The accumulated data demonstrated that the process was sensitive to the amount of a catalyst. The effect of solvents was studied with CH_2Cl_2, CH_3CN, EtOH, and under solvent free conditions. Among the screened solvents, EtOH was the most efficient. In this media the Paal–

Table 2. Synthesis of pyrrole derivatives with STA and SSTA



R	*Method a*		*Method b*	
	time, h	yield, %	time, min	yield, %
H	2	91	75	95
4-Me	2 : 30	94	70	91
4-Cl	5	89	180	91
3-Cl	4 : 40	86	240	87
4-OMe	0.8	95	65	95
4-OEt	0.8	97	20	95
3-Me	2 : 50	93	90	91
2-OH	0.2	90	15	90
3-OH	0.4	90	20	88
4-OH	0.2	91	10	94
$PhCH_2$	0.2	95	5	97

Knorr reaction proceeded smoothly and efficiently particularly under the action of SSTA.

Under the optimized conditions aliphatic and aromatic amines gave pyrrole derivatives in high to excellent yields. Reaction of anilines with an electron-donating group led to the corresponding products in high yield within short time (Table 2).

The recovered STA and SSTA were washed with ethanol (3 × 10 mL), dried at 100°C for 1 h and reused in a subsequent reaction. The catalysts exhibited high catalytic activity after four consecutive runs (80% STA and 89% SSTA).

CONCLUSIONS

The highly efficient one-pot synthesis of pyrrol derivatives by the Pall-Knorr reaction of 2,5-hexadione with aromatic aldehydes catalyzed by STA or SSTA in ethanol is developed.

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