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Magnetic nanosphere Fe_3O_4@SiO_2.$SnCl_4$ promoted synthesis of 5-substituted 1*H*-tetrazoles

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ABSTRACT

Tetrazoles have many interesting futures and applications in drug and energy industries. 5-Substituted 1*H*-tetrazoles were synthesized via [2+3] cycloaddition reaction of aryl or alkyl nitriles with sodium azide in the presence of Fe_3O_4@SiO_2.$SnCl_4$ as catalyst in DMF under reflux conditions. The catalyst was removed from reaction mixture by an external magnet and was reusable for many times without any appreciable loss of its activity. The Fe_3O_4@SiO_2.$SnCl_4$ promotes synthesis of tetrazole in shorter time than other reported catalysts. The obtained tetrazoles were identified by spectroscopic and physical data such as FT-IR, ^{1}HNMR and melting point. Easy workup and reusability of catalyst are some advantages of this protocol.

***Keywords**: Fe_3O_4@SiO_2.$SnCl_4$, 1H-tetrazoles, Organonitrile compounds, Sodium azide, Magnetic catalyst, Lewis acid catalyst.*

1. Introduction

Tetrazole rings have interesting features such as high melting point [1], interesting resonance [2], ionization potential ~11.2 ev [3] and low acidity (K= 1.28 *10^{-5}) [4]. These features tetrazoles rings causes wide range of application such as lipophilic spacers [5], cis-peptide bond mimics [6], ion and peptide chelating agents [7] and metabolically stable surrogates for carboxylic acids [8], ligands [9], antifoggants [10], information recording systems [11], high density energy materials [12] and explosives and green fuel [13]. Meanwhile, anti-arrhythmic [14], anti-diabetic [15], antifungal [16] and antiviral [17] drugs have tetrazoles moiety in their structures. The common method for synthesis of 1*H*-tetrazole derivatives is [2+3] cycloaddition reaction of azide ion with alkyl or aryl nitriles. Previously, various catalysts such as CAES (Cu(II) immobilized on aminated epichlorohydrin activated silica) [18], Cu-MCM-41 nanoparticles [19], Cu(II) immobilized on Fe_3O_4@SiO_2@L-arginine [20], Ni-SMTU@ boehmite [21], Zn/Al hydrotalcite [22], SiO_2-H_3BO_3 [23], $AgNO_3$ [24], gold nano particles and uric chloride [25], $B(C_6F_5)_3$ [26], $PbCl_2$ [27], Zn-Cu alloy [28], AgNPs [29], $Ln(OTf)_3$-SiO_2 [30], TCT (2,4,6-trichloro-1,3,5-triazine) [31], ZnS nanoparticles [32] and nano-$TiCl_4$.SiO_2 [33] have been used for this protocol.

In this work, we wish to report efficient and eco-friendly procedure for the preparation of 5-substituted 1*H*-tetrazoles in the presence of Fe_3O_4@SiO_2.$SnCl_4$ [34,35].

2. Experimental

2.1. General

The chemicals were used without any additional purification. The products were characterized by FT-IR, ^{1}HNMR, and a comparison of their physical properties with those reported in the literature. FT-IR spectra were run on a Bruker, Eqinox 55 spectrometer. A Bruker (DRX-400 Avance) NMR was used to record the ^{1}HNMR spectra. Melting points were determined by a Buchi melting point B-540 B.V.CHI apparatus. BANDELIN Sonopuls HD 3200 ultrasonic apparatus (20 kHz, 150 W) was used for sonication. The microwave oven Kenwood, 1300 W and Mixer Mill (MM 400) in 25 Hz frequency were used for running the described reactions.

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2.2. Synthesis of Magnetic nanosphere Fe_3O_4@SiO_2.$SnCl_4$

In first step, the Fe_3O_4 MNPs (1 g) were diluted by water (20 mL), ethanol (60 mL), and concentrated aqueous ammonia (2 mL, 25 wt%). The resultant dispersion was homogenized in ultrasonic condition. A solution of silicium tetrachloride (1 mL) in ethanol (10 mL) was then drop-wise added to the dispersion at room temperature with vigorous stirring for 15 h. Fe_3O_4@SiO_2 was collected by an external magnet, washed with ethanol (30 mL) and dried under vacuum at 70 ˚C for 5 h. In second step, Fe_3O_4@SiO_2 (0.5 g) was dispersed in $CHCl_3$ (10 mL) under ultrasonic condition for 20 min. Subsequently, $SnCl_4$ (0.5 mL) was added drop-wise to dispersed solution of Fe_3O_4@SiO_2 at room temperature with stirring for 30 min. The resulting suspension was separated using an external magnet, washed with chloroform (20 mL) and dried at room temperature to obtain nano Fe_3O_4@SiO_2.$SnCl_4$as brown solid.

2.3. General procedure for the preparation of 1H-tetrazoles

Sodium azide (1mmol) and a nitrile (1mmol) was mixed in DMF (3 ml). The Fe_3O_4@SiO_2.$SnCl_4$ (0.02- 0.07 g) was added to mixture with stirring under reflux condition. The progress of reaction was monitored by TLC.

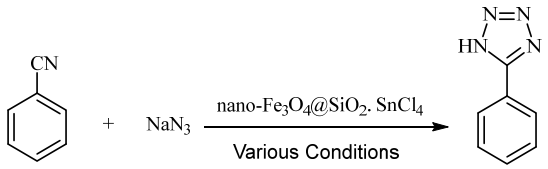
After completion of reaction, the mixture was cooled to room temperature. The catalyst was separated by an external magnet and washed with DMF. Then, the solvent of mixture was removed to obtain a concentrated one. By adding ice water and HCl (37%) to concentrated mixture, a white solid was obtained by scratching. The obtained solid was washed with cold chloroform and crystallized in mixture of water and ethanol.

3. Results and Discussion

Initially, to develop the best reaction conditions, different solvents and conditions were screened for the preparation of 5-substituted 1*H*-tetrazole from the reaction of benzonitrile with sodium azide in the presence of nano-Fe_3O_4@SiO_2.$SnCl_4$ and the results are summarized in Table 1.

Among the different solvents screened, DMF gave the product in good yield at reflux temperature (Table 1, entry 2). Other solvents such as water or polyethyleneglycole (PEG) gave the desired products in low yields (Table 1, entries 4-6). On the other hand, the product was formed in 50 % when the reaction was performed under solvent-free conditions (Table 1, entry 3). In addition, we have tried to reaction of benzonitrile with sodium azide using mixer mill, ultrasonic and microwave, but these conditions did not give the product in good yield (Table 1, entries 7-9).

Table 1. Synthesis of 5-phenyl-1*H*-tetrazole in the presence of nano-Fe_3O_4@SiO_2.$SnCl_4$ in various conditions.[a]

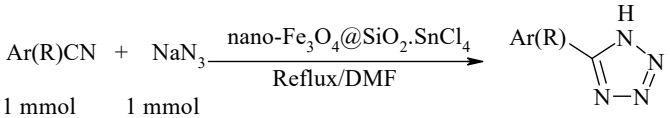


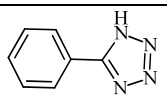
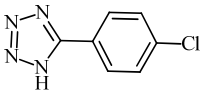
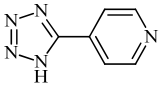
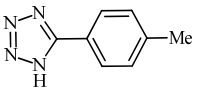
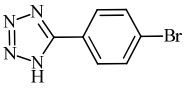
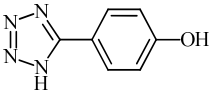
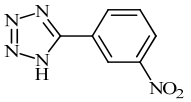
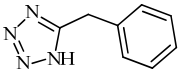
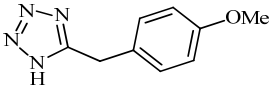
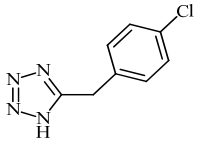
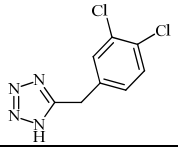
Entry	Solvent	Condition	Time (min)	Yield (%)
1	DMSO	Reflux	120	85
2	DMF	Reflux	66	90
3	-	150-180 °C	180	50
4	PEG	Reflux	300	30
5	Water	Reflux	360	0
6	PEG/water	Reflux	300	15
7	Ethanol/water	Microwave	6	40
8	DMF	Ultrasonic	120	30
9	-	Mixer Mill	15	0

[a]The ratio of benzonitrile (mmol): sodium azide (mmol): nano-Fe_3O_4@SiO_2.$SnCl_4$ (g) is equal to 1:1:0.02.

Under the optimized reaction conditions, we have chosen a variety of structurally divergent benzonitriles to explore the scope and generality of the nano-Fe_3O_4@SiO_2.$SnCl_4$ promoted [2+3] cycloaddition reaction to form 5-substituted 1*H*-tetrazoles and the results are presented in Table 2. It seems that the nature of substituent on the aromatic ring of benzonitriles exert different influences. The electron-withdrawing groups that increase the polarity of the cyanide group inductively (Table 2, entry 7) give higher yields of products compared to the electron-donating groups (Table 2, entry 6). Different halogen substituted benzonitriles, such as 4-chlorobenzonitrile and 4-bromobenzonitrile reacted smoothly and gave the desired products in lower yields (Table 2, entries 2 and 5). Heteroaromatic nitriles such as 2-pyridinecarbonitrile gave the corresponding tetrazoles in shorter reaction times with excellent yields (Table 2, entry 3). Benzilic nitriles (Table 2, entries 8-11) have produced corresponding tetrazoles in good yields (71-80 %).

Table 2. Synthesis of 5-substituted 1*H*-tetrazole derivatives by nano-Fe_3O_4@SiO_2.$SnCl_4$ in DMF under reflux condition.



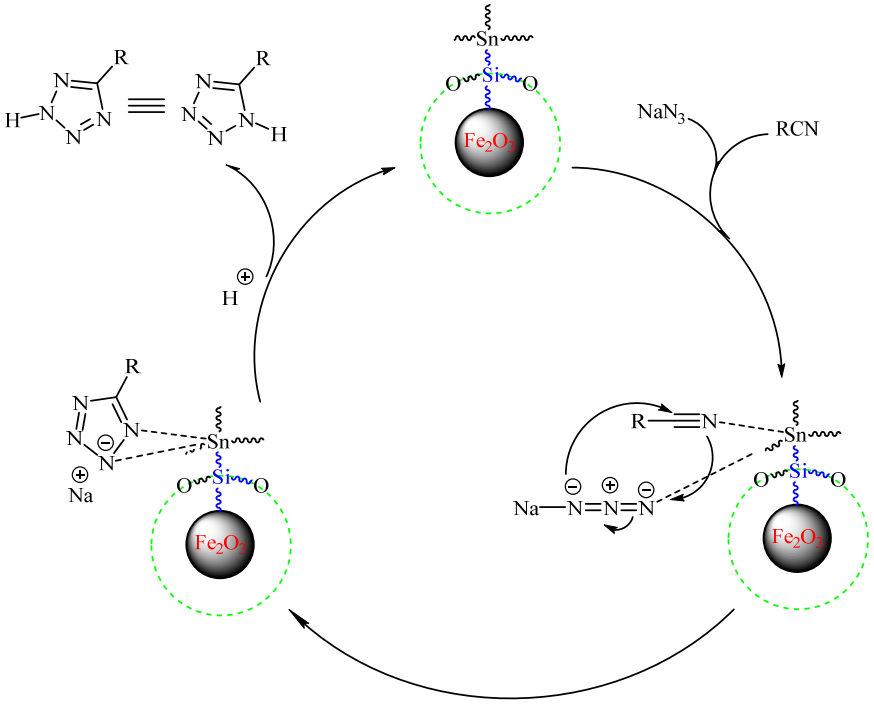
Entry	Ar (R)	Product	Time (h)	Catalyst (g)	Yield[a] (%)	m.p. (°C)		Ref.
						Found	Reported	
1	Ph		1.1	0.02	90	215-217	214-216	[20]
2	4-Cl-Ph		2	0.04	90	258-259	261-262	[20]
3	4-Pyridyl		1.75	0.03	93	254-256	255-258	[18]
4	4-Me-Ph		1	0.03	80	249-250	242-245	[21]
5	4-Br-Ph		1.5	0.04	90	264-265	264-264	[20]
6	4-OH-Ph		3	0.04	88	233-234	233-234	[18]
7	3-NO_2-Ph		0.75	0.03	92	217–220	215–219	[33]
8	$PhCH_2$		3	0.05	80	118-120	120-123	[21]
9	4-OMe-$PhCH_2$		6	0.06	71	231–232	232–233	[33]
10	4-Cl-$PhCH_2$		3	0.04	76	260–261	260–261	[33]
11	3,4-Cl_2-Ph		5	0.07	71	151-152	128–130	[33]

[a]Isolated yield.

Our proposed mechanism for preparation of 5-substituted-1*H*-tetrazoles was shown in scheme 1. In this protocol, Sn Lewis acid has activated organonitrile compounds as electrophile. Meanwhile, Sn in catalyst has attracted azide ion in near of activated organonitrile compound for rapid interaction between organonitrile and azide ion.

In comparison between our protocol and other reported ones (Table 3), we have found that nano Fe_3O_4@SiO_2.$SnCl_4$ promotes synthesis of tetrazole in shorter time. The workup of reaction is very simple and the catalyst is removable very fast from reaction mixture by an external magnet.

Meanwhile, the nano Fe_3O_4@SiO_2.$SnCl_4$ is prepared by a simple procedure and is cheaper than other catalyst such as MZNSS, Ni-SMTU@boehmite, Cu(II) immobilized on Fe_3O_4@SiO_2@L-arginine and $AgNO_3$.



Scheme 1. Proposed mechanism for preparation of 1*H*-tetrazoles in the presence of nano-Fe_3O_4@SiO_2.$SnCl_4$.

Table 3. Synthesis of 5-phenyl-1*H*-tetrazole in the presence of various catalysts.

Entry	Catal., g [mol%]	Nitrile:NaN_3 (mmol)	Solvent/Condition	Time (h)	Yield (%)[a]	Ref.
1	Nano Fe_3O_4@SiO_2.$SnCl_4$, 0.02	1:1	DMF/Reflux	1.1	90	This work
2	Nano ZnO, 0.04	1:1.1	DMF/120 °C	12-14	72	36
3	Zn/Al, 0.05	1:1.5	DMF/120 °C	12	84	37
4	$FeCl_3/SiO_2$, 0.045	1:1.5	DMF/120 °C	12	79	38
5	MZNSS[b], 0.04	1:2	DMF/120 °C	36	96	39
6	Ni-SMTU[c]@boehmite, 0.025	1:1.4	PEG 400, 120 °C	1.5	94	21
7	Cu(II) immobilized on Fe_3O_4@SiO_2@L-arginine, 0.03	1:1	PEG 400, 120 °C	6	97	20
8	$AgNO_3$, [10]	1:1.5	DMF/120 °C	5	83	24

[a]Isolated yield.
[b]Mesoporous ZnS nanospheres.
[c]Ni-S-methylisothiourea complex supported on boehmite.

The reusability of the catalyst is an important benefit and make it useful for commercial applications. Thus, after the completion of the reaction, the catalyst was separated and washed with ethanol and then chloroform and dried at room temperature. The isolated catalyst was used for the next run in current reaction under identical condition. The catalyst could be reused for four times (The yields were 90, 87, 85 and 82%, respectively) without any appreciable loss of its activity.

4. Conclusion

We have demonstrated a simple method for the preparation of 5-substituted -1*H*-tetrazole derivatives using Fe_3O_4@SiO_2.$SnCl_4$ as eco-friendly and efficient catalyst in a one-pot procedure. Short reaction times, high yields, a clean process, simple methodology, easy work-up and green conditions are advantages of this protocol.

Acknowledgements

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