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Synthesis of 1, 4 Benzodiazine Derivatives by New Catalytic Method

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Abstract:
Silica-supported stannic tetra chloride as novel heterogeneous catalyst for the acid-catalyzed reactions, substituted 1,4 benzodiazine hetro cyclic condensation. It was used as an heterogeneous condensation of 1, 2 diamine with different substituted aryl carbonyl compound at room temperature in presence of solvent DCM (Dichloromethane). This method was proved to be simple, convenient and the product was isolated with good yield.

Keywords: *Sncl4/ Sio2, aryl 1, 2 demine, 1, 2 dicarbonyl, DCM, RT.*

1. Introduction

1, 4 benzodiazine or quinoxaline nitrogen containing moiety is an important nucleus in organic synthesis which has been extensively used in synthetic organic chemistry, pharmaceutical and in medicine[1-4]. A Wide range important organic reaction can be efficiently catalyzed by supported solid acids materials which can be to provide different types of acidity as well as high degree of reaction selectivity. The use of lewis solid acid with silica-supported acts as a eco-friendly and reusable, environmentally acceptable heterogeneous catalyst has increased in heterocyclic synthesis and pharmaceutical chemical industries during the last couple of decades[5-6].silica supported stannic chloride is a mild solid lewis acid that promotes acid catalyzed organic reactions this catalyst Has been previously applied to the one pot synthesis of p-acetamidoketones, acylals and silylation of hydroxyl groups[6-9].The use of lewis acid supported reagents[10-11] have received considerable importance in chemical transformation because of their high efficient catalytic activity enhanced rate of reactions, short reaction time, and grater selectivity of catalyst[11-12] a few catalytic reactions for the preparation of these compounds have been recently reported in the literature[12-19]. In records stannous chloride has been used as a catalyst because this tin halides not only is commercially available and inexpensive but also is easy to handle then other metal halides such as $Incl_3$, $Gdcl_3$, $Ticl_4$[20]. In the present work we used here in silica supported stannic tetra chloride catalyst for the synthesis of Substituted 1,4 benzodiazine through heterolytic condensation of 1,2 diamine with 1,2 dicarbonly in presence of solvent dichloromethane at room temperature is an acid catalyzed reaction. Although these heterocycles have numerous applications in pharmaceuticals and medicine[21]. This method was proved to be simple, convenient and the product was isolated with good yield.

2. Materials and Method

All chemicals were purchased from Merck, Aldrich and Rankem chemical companies and used without further purification. The uncorrected melting points of compounds were taken in an open capillary in a paraffin bath. The progresses of the reaction were monitored by thin layer chromatography (TLC). IR spectra were recorded on Perkin Elmer FT spectrophotometer in KBr disc. ^1H NMR spectra were recorded on an 500 MHz FT-NMR spectrometer in $CDCl_3$ and DMSO-d_6 as a solvent and chemical shift values are recorded in units (δ) relative to tetramethylsilane (Me_4Si) as an internal standard (Figure 1).

2.1. Preparation of $SnCL_4/SIO_2$ catalyst

Stannic chloride(2mmol) was added to a suspension of sio_2 silica (300-400mesh,27.8g) in dichloromethane solvent(50ml).the mixture was stirred at room temperature for 2h.the solvent was removed with rotatory evaporator and the residue was heated at 150c under vacuum for 2.5h to furnish $sncl_4/sio_2$ as a free flowing powder.

2.2. General Procedure

A mixture of aryl 1, 2 diamine (2 mmol) 1,2 dicarbonyl (1 mmol) and $Sncl_4/Sio_2$ (5 mmol) was taken in RBF and stirred at room temperature for the appropriate reaction time (Table 2). After completion o f the reaction (monitored by TLC using ethyl acetate/hexane3:7) the organic medium was removed with rotatory evaporator under reduced pressure. Dichloromethane was added to

the resulting solid mixture. The catalyst was removed by filtration and the solvent CH_2CL_2 was evaporated to afford the final product 1.the crude product were crystallized from ethanol to obtained pure solid product. All the isolated products were characterized by ^{1}HNMR ^{13}C NMR and MS spectral analysis.

2.3. Spectral Data

6-nitro 2,3-diphenyl 1,4-benzodiazine(1a);mp 190-200c^0 ^{1}HNMR(500 MHz, $CDCL_3$) :7.25(m, 6H) 6.99(d,4H) 7.1(d,1H) 8.10(d,1H) ^{13}CNMR (100 MHz $CDCL_3$) 128.30, 128.40, 129.40, 130.36, 129.53, 128.40,129.54, 130.62, 130.70, 131.20, 137.10, 131.80, 136.12, 138.10, 139.18, 140.32, 141.80, 150.32, 153.52m MS (EI) m/z(%) 267(M+100)

6-chloro-2,3 diphenyl 1,4 benzodiazine (1c);mp 156-159c^0 ^{1}HNMR (500 MHz, $CDCL_3$) 7.00(m 6H), 7.50{d, 4H}, 7.68(d,1H), 7.92(d,1H), 8.04(d,1H); ^{13}CNMR (100 MHz, $CDCL_3$) :128.50,128.52,128.72,129.30, 129.30, 129.52, 130.20, 130.56, 130.82, 131.22, 131.40, 136.02, 136.10, 139.8, 139.17, 140.10, 141.84, 154.02, 154.62; MS(EI) m/z (%)315 (m+ 100) 278

6-methyl -2,3 diphenyl(2-methoxy phenyl) 1,4benzodiazine(1f);mp 165-180c ^{0} ^{1}HNMR(500 MHz,$CDCL_3$) 3.70(s,6H) 6.20(d,3H) 7.00(d,4H), 7.42(d,4H),7.80(dd,2H), 8.15(dd,2H); ^{13}CNMR (100 MHz $CDCL_3$) : 50.62,55.40, 55.74, 110.20, 114.30, 128.10, 128.32, 128.36, 128.50, 130.64, 130.70, 130.94, 131.74,131.76, 132.86, 135.50, 139.80, 141.62, 153.50, 154.20,160.70, 160.90, MS (EI) m/z (%) 365(M+100)352.

3. Result and Discussion

In this study, various solid supports lewis acid with stannic chloride were tested for the same reaction

Entry	Catalyst	Conversion (%)
1	-----	02
2	Sio_2 activated	25
2	$Sbcl_3$	50
4	$SnCl_2$. H_2o	80
5	$SnCl_4/Sio_2$	90

Table 1: Catalyst tested of heterogeneous/supported lewis acid sites on the synthesis of (1a) product

According to above results all catalyst actively participated in chemical reactions except silica alone revealed poor catalytic activity. Silica-supported stannic chloride efficiently catalyzed the reactions to afford the desired products compared with other supported lewis acids as above (table 2} It shows high efficiency and reusability of catalyst for the synthesis of a various substituted 1,4 benzodiazine in good yield at room temperature in both electron efficient as well as electron deficient species. Electron withdrawing groups enhanced the rate of reaction as compare to the electron donating group .this method offers some advantage in terms of simplicity of performance. Heterogeneous catalyst acts as eco-friendly for a variety of organic transformations. This method not only gave the products in good yields, but also avoid the problems associated with catalyst cost, handling, reduced time, safety & pollution.

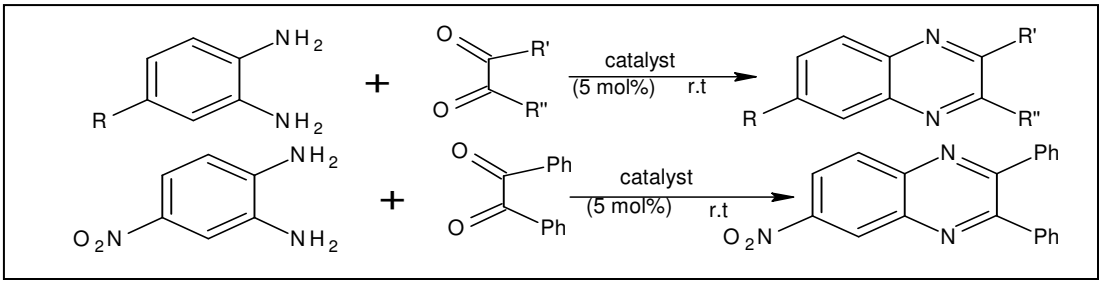

Figure 1

Compound	R	R^I	R^{II}	Time	Yields	M.P (C^0)
1a	No_2	Ph	Ph	2 h	96%	190-200
1b	Me	Ph	Ph	10 min	90%	154-158
1c	Cl	Ph	Ph	15 min	94%	156-159
1d	H	Ph	Ph	40 min	95%	130-150
1e	H	4(Meo)ph	4(Meo)-ph	30 min	89%	153-160
1f	Me	2(Meo)ph	2(Meo)-ph	25 min	90%	165-180
1g	Cl	2(Meo)ph	2(Meo)-ph	3 h	95%	160-165
1h	H	Me	Me	10 min	90%	102-104
1i	Cl	Me	Me	10 min	94%	120-125
1j	No_2	Me	Me	15 min	97%	180-195

Table 2: $Sncl_4/Sio_2$ catalyzed synthesis of substituted 1, 4 benzodiazine :

4. Conclusion

Silica- supported stannic tetra chloride is prepared and characterized as heterogeneous lewis acid catalyst in an example it shows high efficiency and greater selectivity for the synthesis of various substituted 1, 4 benzodiazine derivatives heterocycles in good yields at room temperature. This protocol offers many attractive features such as reduces reaction time, higher yields & economic viability of the catalyst. This method was to proved to be simple convenient and user friendly for the synthesis of various substituted biological and pharmaceutical important heterocyclic compound.

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