Indian Journal of Science and Technology, *Vol 8(11), 68669, June 2015*
ISSN (Print) : 0974-6846
ISSN (Online) : 0974-5645

Synthesis of Spiro Pyran by using Silica-Bonded N-Propyldiethylenetriamine as Recyclable Basic Catalyst

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Abstract

In some natural products isatin and its derivatives used as a precursors due to the wonderful biological characteristics. In the biological research, we can raise the biocidal activity with the entity of two or more various heterocyclic moieties in one molecule. In continuation of our work to develop new catalysts for organic transformations, here we are reported the preparation of spirooxindole derivatives. Basis of our method, using of the isatin reaction and malononitrie. Also, in this method, impressible and recyclable catalysts are silica-bonded N-propyldiethylenetriamine and silica-bonded N-propyl diethylenetriamine sulfamic acid. Result showed that, this method has many advantages like as simple work-up method, clean and facile procedure, and environment friendly circumstance.

Keywords: Isatin, Spirooxindoles, Spiro Pyran, Three-component, Water

1. Introduction

In recent years, multi-component reactions have high potential application in combinatorial chemistry due to the ability to preparation main compounds with greater output, as well as multi-component reactions, suggestion the benefit of easiness and combinatory efficiency over arbitrary chemical reaction. Expansion and application of these multi-component coupling reaction in watery medium are favorable, as they equipped easy and quick access to many organic molecules through a tolerable path[1,2]. Isatin and its derivatives have many application due to the wonderful biological characteristics and are broadly used as precursors[3–5]. In the biological research, we can raised the biocidal activity with the entity of two or more various heterocyclic moieties in single molecule[6–8]. It was predestinated the preparation of a series of spirooxindoles with molten chromenes. In this process three-component of reaction like as isatin, or acenaphthoquinone, malononitrile or ethylcyanoacetate, and 1,3-dicarbonyl compounds are used. All of reactions considered in the exictance of catalytic ammonium chloride under watery circumstances. Molten chromenes have received more attention because to their high potential application and useful biological characteristics, antianaphylactic that comprise diuretic, anticancer, spasmolitic, anticoagulant[9–13]. In recent years many reports on multi-component studies to the preparation of spirooxindoles, Shanthi et al. studied a three component condensation of cyclic 1,3-diketones, isatin, and malononitrile catalyzed by 20 mol % of $InCl_3$[14], using electrochemical methods for preparation of spirooxindoles[15] that tolerate from technical complexity. In water medium, this process was carried out in the existence of the surfactant triethylbenzylammonium chloride[16]. Also, this method has a significant disadvantage due to the production of mixtures unsaturated nitriles and pyrans. The three component Et_3N-catalyzed method for the synthetic preparation

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of 2-amino-spiro pyrans under simple conditions have been described[17]. In this procedure, it utilizes a suitable and available acidic catalyst (NH_4Cl) and water for these transfigurations. This treatment is very adequate and would be beneficial for the preparation of various kinds of spirooxindoles.

2. Experimental

In first step of experimental section, we produced the mixture from following materials.

1. Isatin (1 mmol).
2. Malononitrile (1 mmol).
3. 5,5-bis-substituted-1,3-cyclohexanedione (1 mmol).
4. SBNPTT (0.05 gr).

All of materials for 10 hours in H_2O (5 mL) was stirred. Upon accomplishment monitored by TLC, the final mixture was cooled down then filtered. In warm ethanol, the remaining mixture was dissolved and filtered, and then to separate catalyst, mixture was washed again with warm ethanol (2×5 mL). After cooling ethanol the product was precipitated and filtered. For further purification the product was recrystallized from ethanol.

3. Result

In this experimental work, assessment of various catalysts and different solvent, we have described that SBNPTT has a special ability to raise the reaction rate in aqueous medium. Model of this reaction is the reaction of 5,5-bis-substituted-1,3-cyclohexanedione, malononitrile and isatin in the presence of SBNPTT in water (Table 1). The interesting results were generated in water as solvent (Table 2). The optimal amounts are as follow:

1. Molar ratio of 1:1:1 in the presence of catalytic SBNPTT
2. Water at return conditions for 35 minute (Figure 1) furnished spirooxindoles in moderate yields (Table 3).

4. Conclusion

Spiro compounds are an important class of materials that are found naturally, and many biological properties are expressed. Biological and therapeutic activity of these compounds can be anti-cancer, anti-coagulation, urine collection, and anticonvulsants they noted. Many of the elders are Spiro that have analgesic activity, herbicides,

Table 1. Solvent effects on the reaction of 5,5-bis-substituted-1,3-cyclohexanedione (1), isatin (2), and malononitrile (3) in the presence of 0.05 gr SBNPTT at reflux conditions

Entry	Solvent	Time(min)	Yield(%)
1	CH_3OH	490	60
2	C_2H_5OH	325	55
3	CH_3CN	420	25
4	CH_3Cl	450	Trace
5	CH_2Cl_2	400	Trace
6	Solvent-free	600	Trace
7	H_2O	35	85

Table 2. Synthesis of spirooxindoles using various SBNPTT

Entry	The Amount of Catalyst(gr)	Time (min)	Yield (%)
1	0.01	120	75
2	0.03	80	70
3	0.05	35	85
4	0.07	40	80
5	0.1	85	82

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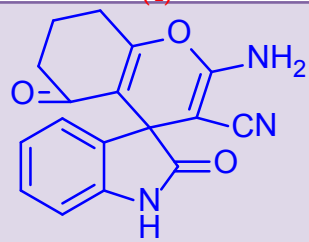
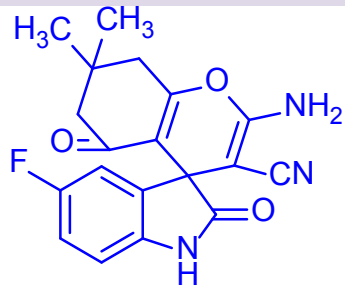
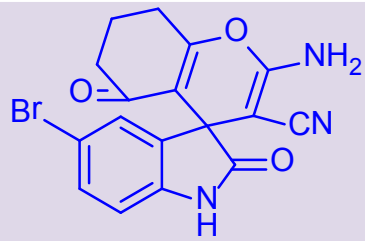
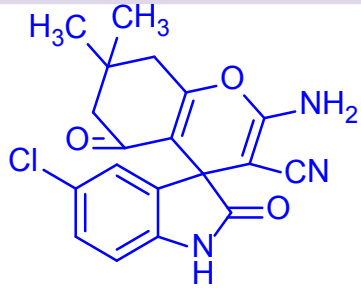
Table 3. Synthesis of spirooxindoles in water by the reaction of 5,5-bis-substituted-1,3-cyclohexanedione (1), isatins (2), and malononitrile (3) in the presence of SBNPTT

Entry	Product (4)	Time (min)	Yield (%)	Mp (°C)
1		35	90	270-272
2		42	86	285-287
3		32	85	280-282
4		28	81	290-292

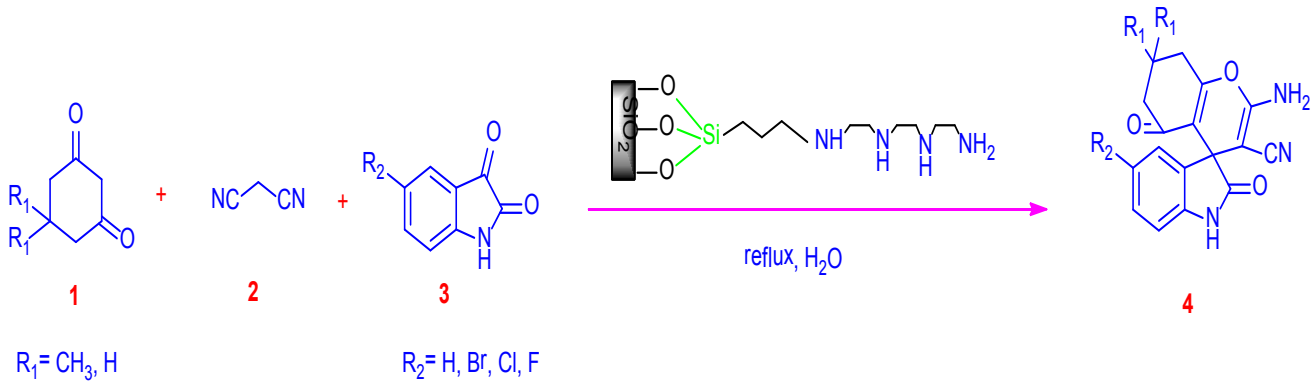


Figure 1. Synthesis of spirooxindoles in water by the reaction of 5,5-bis-substituted-1,3-cyclohexanedione (1), isatins (2), and malononitrie (3) in the presence of SBNPTT.

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