Bull. Chem. Soc. Ethiop. **2016**, 30(1), 129-136.
Printed in Ethiopia
DOI: http://dx.doi.org/10.4314/bcse.v30i1.12
ISSN 1011-3924

SYNTHESIS OF *BIS*-QUINOXALINE DERIVATIVES USING TONSIL CLAY AS A CATALYST

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(Received May 16, 2015; revised January 3, 2016)

ABSTRACT. A convenient and efficient synthesis of new *bis*-quinoxaline is described, involving condensation of 1,2-diamines with 9-ethyl-3,6-di(1,2-dioxoethyl)carbazole in the presence of Tonsil clay, a readily available and inexpensive catalyst. The structures of all new products were identified by ^{1}H-NMR, ^{13}C-NMR and FT-IR spectral data and microanalysis.

KEY WORDS: *bis*-Quinoxaline, *bis*-Glyoxal, Green chemistry, 1,2-Diamine, Tonsil clay

INTRODUCTION

Quinoxaline derivatives have shown a broad spectrum of biological activity including anti-bacterial, antiviral, anti-inflammatory, kinas inhibitory and anti-cancer activities [1]. A number of synthetic strategies have been developed for the preparation of substituted quinoxalines [2]. The most common method relies on the condensation of an aryl 1,2-diamine with a 1,2-dicarbonyl compound in refluxing ethanol or acetic acid for 2-12 h giving 34-85% yields [3]. Recently, improved methods have been reported by using different catalysts [4-9]. The synthetic protocol has been further improved by using 1,2-diketone alternatives, such as epoxides [10], α-bromoketones [7b, 7c, 11] and α-hydroxy ketones [12].

However, most of these processes suffer from a variety of disadvantages which limit their use as environmentally benign processes, such as being polluting, having high cost, poor chemical yields, and a requirement for long reaction times, harsh reaction conditions and tedious work-up procedure.

In continuation of our studies on the development of new routes for the synthesis of heterocyclic compounds using aryl glyoxals [13-18], we herein report the synthesis of new *bis*-quinoxaline derivatives from the glyoxal, 9-ethyl-3,6-di(1,2-dioxoethyl)carbazole **(1)**, and 1,2-diamines **(2)** in the presence of the Bentonite clay, Tonsil, as catalyst in solvent free conditions or in ethanol/DMF solvents at reflux (Scheme 1).

We have previously reported the synthesis of *bis*-glyoxal **(1)** by the reaction of 3,6-diacetyl-9-ethylcarbazole with several oxidizing agents in good yields [19]. Tonsil clay has never been used in quinoxaline synthesis as a heterogeneous catalyst, and can be separated by simple filtration and be recycled.

Clays are very cheap, commercially available, green and heterogeneous reagents which have been used in various organic transformations such as Biginelli condensation [20], Baeyer-Villiger oxidation of ketones [21], anti-Markonikov hydroamination of α,β-ethylenic compounds [22], epoxidation of alkene and hydroxylation of alkanes [23], synthesis of 1,2,3,4-tetrahydrocarbazoles and indoles [24], Friedel-Crafts type benzylation reactions [25], ring

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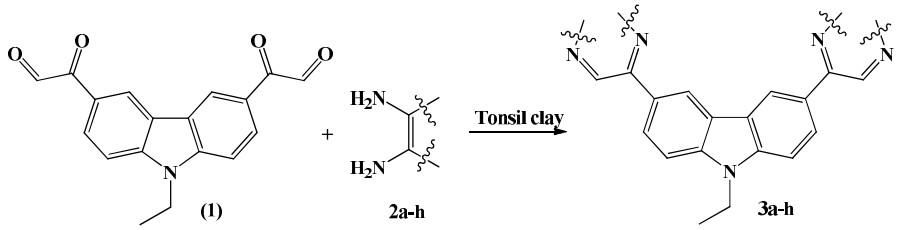
opening of epoxides with thiols [26], synthesis of *bis*-phthalimides [27], synthesis of 2-aryl-1-aryl-1*H*-1,3-benzimidazole [28], and Michael reaction of amines [29], among others.



Scheme 1. The reaction of 1,2-diamine with bis-aryl glyoxal in presence of Tonsil.

EXPERIMENTAL

Tonsil, cheap Bentonitic clay, is readily available commercially. This clay was shown to have the following composition (in %): SiO_2: 74.5, Al_2O_3: 9.3, MgO: 0.4, Fe_2O_3: 1.3, CaO: 4.0, K_2O: 0.4 and H_2O: 9.7. All solvents were purified before use by standard purification methods. The organic extracts were dried with anhydrous sodium sulfate. All the diamines were purchased from Fluka or Merck. Melting points were recorded on a Philips Harris C4954718 apparatus and are not corrected. Infrared spectra were measured with a Bruker FT-IR spectrometer using KBr disks. ^{1}H-NMR spectra were recorded on a Bruker spectrometer (300 MHz). ^{13}C-NMR spectra were recorded on a 75 MHz spectrometer from Bruker. All measurements were made in duterated chloroform and dimethyl sulfoxide. Analytical thin layer chromatography (TLC) was carried out on precoated aluminium sheet with silica gel 60 F_{254} obtained from Merck and detection was made with the help of a UV lamp (λ 254 nm). Elemental analyses were performed on a Leco Analyzer 932.

General procedure for the synthesis of bis-quinoxaline derivatives in the solid phase state with Tonsil catalyst

A mixture of the 1,2-diamine (10 mmol), *bis*-glyoxal **(1)** (5 mmol) and Tonsil catalyst (2 g) was prepared in a mortar and pestle by grinding them together at room temperature as reported in Tables 1 and 2. In cases when the mixture stuck to the walls of the mortar, it was taken off the walls with a spatula and grinding was continued. The mixture was warmed with DMF (5 mL), filtered, and the filtrate diluted with water (2 mL). The solid product was recrystallized from ethanol to afford to pure *bis*-quinoxaline derivatives.

General procedure for the synthesis of bis-quinoxaline derivatives in EtOH/DMF using Tonsil catalyst

A mixture of the 1,2-diamine (2 mmol), *bis*-glyoxal **(1)** (1 mmol) and Tonsil catalyst (0.5 g) in *N*,*N*-dimethylformamide (1 mL) and ethanol (3 mL) was heated at 90 ^{o}C. The progress of reaction was monitored by TLC using $CHCl_3$/MeOH/EtOAc (10:1:2) as eluent. After completion (as show in Table 2), the catalyst was recovered by filtration and washed with a small amount of hot *N*,*N*-dimethylformamide. The cooled filtrate was diluted with cold water (2 mL) and the precipitate was collected, washed with cold ethanol and recrystallized from ethanol to afford the pure *bis*-quinoxaline derivatives.

*9-Ethyl-3,6-bis(quinoxalin-2-yl)-9H-carbazole (**3a**)*. This compound was obtained as yellow solid, m.p. 190-192 ^{o}C. ^{1}H NMR ($CDCl_3$) ppm δ: 1.53 (t, J = 7.2 Hz, 3H, CH_3), 4.45 (q, J = 7.2 Hz, 2H, CH_2) and 7.57-9.51 (m, 16H, Ar). ^{13}C NMR ($CDCl_3$) ppm δ: 13.9, 38.1, 109.5, 120.4, 123.9, 125.8, 128.4, 129.0, 129.1, 129.4, 130.2, 141.2, 141.8, 142.5, 143.5, 152.3. FT-IR (KBr) ν_{max}/cm^{-1}: 3440, 1594, 1542, 1438, 1299, 1235, 757. Anal. calc. for $C_{30}H_{21}N_5$: C, 79.80; H, 4.69; N, 15.51%; found: C, 79.58; H, 4.75; N, 15.67 %.

*9-Ethyl-3,6-bis(6-methylquinoxalin-2-yl)-9H-carbazole (**3b**)*. This compound was obtained as yellow solid, m.p. 215-219 ^{o}C. ^{1}H NMR ($CDCl_3$) ppm δ: 1.52 (t, J = 7.2 Hz, 3H, CH_3), 2.62 (s, 6H), 4.44 (q, J = 7.2 Hz, 2H, CH_2), 7.55-9.45 ppm (m, 14H, Ar). ^{13}C NMR ($CDCl_3$) ppm δ: 13.9, 21.9, 38.0, 109.4, 120.1, 120.2, 123.9, 125.7, 125.7, 128.0, 128.3, 128.5, 128.6, 128.9, 131.2, 132.4, 142.6. FT-IR (KBr) ν_{max}/cm^{-1}: 3435, 3408, 2956, 2925, 1608, 1544, 1480, 1297, 1238, 1140, 815. Anal. calc. for $C_{32}H_{25}N_5$: C, 80.14; H, 5.25; N, 14.60%; found: C, 80.20; H, 5.19; N, 14.61%.

*9-Ethyl-3,6-bis(pyrido[2,3-b]pyrazin-3-yl)-9H-carbazole (**3c**)*. This compound was obtained as brown solid, decomposed about 300 ^{o}C. ^{1}H NMR ($CDCl_3$) ppm δ: 1.56 (t, J = 7.2, 3H, CH_3), 4.52 (q, J = 7.2 Hz, 2H, CH_2), 7.90-9.83 ppm (m, 8H, Ar). ^{13}C NMR ($CDCl_3$) ppm δ: 14.0, 38.2, 109.7, 121.0, 124.0, 124.2, 126.5, 127.5, 136.3, 138.1, 142.4, 144.4, 151.1, 154.3, 155.0. FT-IR (KBr) ν_{max}/cm^{-1}: 3426, 3295, 1545, 1480, 1307, 1248, 1126, 825, 783, 599. Anal. calc. for $C_{28}H_{19}N_7$: C, 74.16; H, 4.22; N, 21.62%; found: C, 74.08; H, 4.25; N, 21.67%.

*9-Ethyl-3,6-bis (pyrido [3,4-b] pyrazin-3-yl)-9H-carbazole (**3d**)*. This compound was obtained as pale yellow solid, m.p. 280-284 ^{o}C. ^{1}H NMR ($CDCl_3$) ppm δ: 1.58 (t, J = 6.3 Hz, 3H, CH_3), 4.54 (q, J = 6.3 Hz, 2H, CH_2) and 7.65-9.72 ppm (m, 14H, Ar); ^{13}C NMR ($CDCl_3$) ppm δ: 14.0, 38.5, 109.9, 121.1, 121.4, 121.6, 124.0, 126.5, 127.7, 142.5, 145.2, 147.9, 154.2, 154.6, 156.1. FT-IR (KBr) ν_{max}/cm^{-1}: 3439, 2929, 1586, 1360, 1236, 1044, 820, 616. Anal. calc. for $C_{28}H_{19}N_7$: C, 74.16; H, 4.22; N, 21.62%; found: C, 74.11; H, 4.27; N, 21.62%.

*2,2'-(9-Ethyl-9H-carbazole-3,6-diyl)bis(quinoxaline-6-sodium sulphonate) (**3e**)*. All attempts to synthesize this product failed under both solid phase or reflux conditions and the starting materials were recovered.

*(9-Ethyl-9H-carbazole-3,6-diyl)bis((2,3-dihydro-1H-perimidin-2-yl)methanone) (**3f**)*. This compound was obtained as dark brown solid, decomposed at 310 ^{o}C. ^{1}H NMR ($CDCl_3$) ppm: δ 1.48 (t, J = 7.2 Hz , 3H, CH_3), 4.38 (q, J = 7.2 Hz , 2H, CH_2), 4.99 (bs, 4H, 4NH, exchange with D_2O) 5.87 (S, 2H, 2CH), 6.35-8.84 (m, 18H, Ar); ^{13}C NMR ($CDCl_3$) ppm: δ 14.3, 38.1, 63.5, 105.0, 110.3, 112.3, 115.6, 119.0, 122.9, 123.6, 126.9, 127.2, 127.8, 128.8, 134.5, 135.5, 141.4, 141.6, 143.4, 196.0. FT-IR (KBr) ν_{max}/cm^{-1}: 3372, 3048, 2932, 1907, 1589, 1470, 1232, 728. Anal. calc. for $C_{38}H_{29}N_5O_2$: C, 77.66; H, 4.97; N, 11.92%; found: C, 77.71; H, 5.01; N, 11.96%.

*5,5'-(9-Ethyl-9H-carbazole-3,6-diyl)bis(pyrazine-2,3-dicarbonitrile) (**3g**)*. This compound was obtained as orange solid, decomposed at 288 ^{o}C. ^{1}H NMR (DMSO-d_6) ppm: δ 1.40 (t, J = 7.2 Hz, 3H, CH_3), 4.58 (q, J = 7.2, 2H, CH_2), 7.90-9.83 (m, 8H, Ar). ^{13}C NMR (DMSO-d_6) ppm δ: 14.4, 38.2, 111.4, 114.6, 115.0, 122.0, 123.5, 124.9, 126.9, 129.8, 133.3, 143.1, 145.1, 154.4. FT-IR (KBr) ν_{max}/cm^{-1}: 3429, 2974, 2938, 2232, 1590, 1541, 1497, 1306, 1128, 817, 572 and 464. Anal. calc. for $C_{26}H_{13}N_9$: C, 69.17; H, 2.90; N, 27.92%; found: C, 69.12; H, 2.93; N, 27.95%.

*9-Ethyl-3,6-bis(5-methyl-5,6-dihydropyrazin-2-yl)-9H-carbazole (**3h**)*. After adding the 1,2-diamine to the reaction mixture of *bis*-glyoxal and Tonsil at -78 ^{o}C or room temperature gave a mixture of unidentifiable materials.

RESULTS AND DISCUSSION

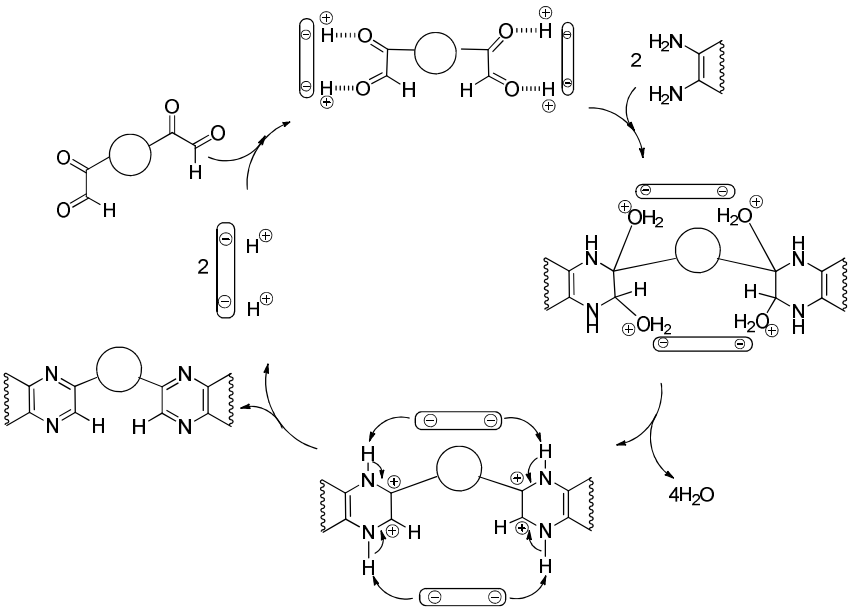
Tonsil clay is a nanoparticle with layered structure. The layers possess net negative charge that is neutralized by cations such as Na^{+}, K^{+}, Ca^{2+}, which occupy the interlamellar space. These cations can be very easily replaced by other cations or other molecules.

To investigate the catalytic capability of Tonsil, the reaction between different 1,2-diamines and *bis*-glyoxal (**1**) to form *bis*-quinoxalines has been utilized, and the results obtained are summarized in Table 1. To illustrate the need for Tonsil in these reactions, the experiment was also conducted in the absence of catalyst. The yields in the absence of catalyst were about 31-80% yield.

As shown in Tables 1 and 2, reaction in EtOH/DMF in the presence of Tonsil gave relatively good yields of product, but required longer reaction times than in the solid state. In the absence of clay, reactions were considerably slower and less efficient.

We believe that Tonsil clay plays role as an acidic catalyst in these reactions and the condensation reaction of 1,2-diamines with 1,2-dicarbonyl compounds under these conditions follows the regular mechanism of acid-catalyzed condensation reactions [30]. The catalyst is stable to air and moisture, nontoxic, and inexpensive. In addition, it can be quantitatively recovered by filtration and reused.

The proposed mechanism of the reaction in presence of Tonsil is shown in Scheme 2.



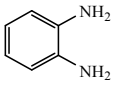
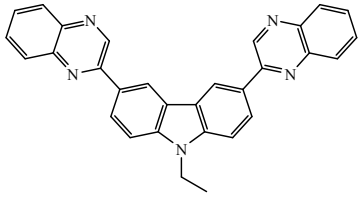
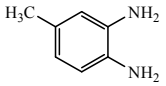
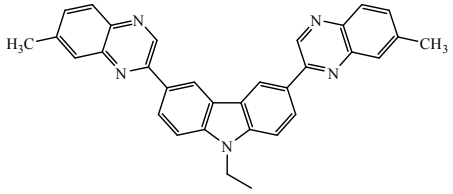
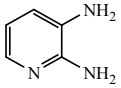
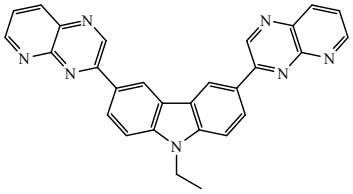
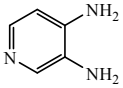
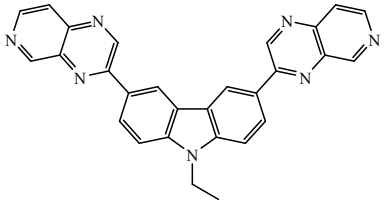
Scheme 2. The proposed mechanism of condensation in the presence of Tonsil as catalyst.

Aromatic1,2-diamines, in particular, afforded good yields. The use of the unsymmetrical diamines (**2b**), (**2c**) and (**2d**) could in principal lead to a number of isomeric products, but the

physical and spectroscopic properties of the product showed that the reactions are regioselective. It seems that in the condensation of *bis*-glyoxal (**1**) with 3,4-diaminotoluene (**2b**), 2,3-diaminopyridine (**2c**) and 3,4-diaminopyridine (**2d**), the more nucleophilic amino group attacks on the glyoxal's formyl groups in the first step, and the condensation of the less reactive amino group with keto groups take place in the second step, leading to the formation of final products (**3b**), (**3c**) and (**3d**), respectively, in a regioselective manner. We have successfully developed a simple, cheap, efficient and ecofriendly method for the synthesis of new *bis*-quinoxaline derivatives from various 1,2-diamines with bis-glyoxal (**1**) using readily available Tonsil clay as catalyst.

The pharmaceutical activates of newly synthesized *bis*-quinoxalines will be examined in comparison with those of our previously prepared mono-quinoxaline derivatives by microbiology section of Daana Pharmaceutical Co. in future.

Table 1. Solvent-free reactions of bis-quinoxaline (1) with 1,2-diamines in presence of Tonsil.

Entry	1,2-Diamine	Product	Time (min)	Yield (%)
1	 (**2a**)	 (**3a**)	15	86
2	 (**2b**)	 (**3b**)	15	79
3	 (**2c**)	 (**3c**)	25	61
4	 (**2d**)	 (**3d**)	20	74

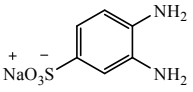
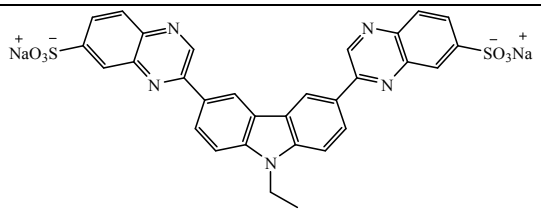
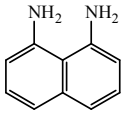
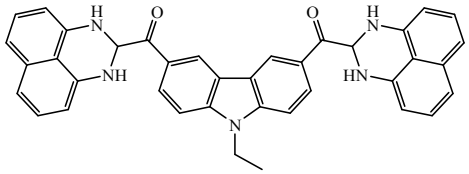
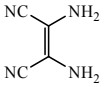
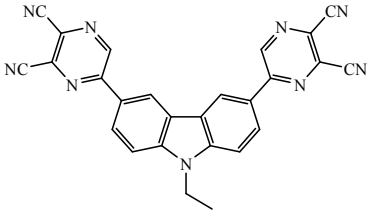
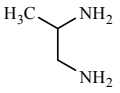
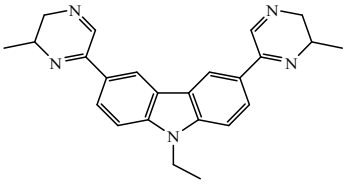
5	 (**2e**)	 (**3e**)	25	N.R
6	 (**2f**)	 (**3f**)	30	54
7	 (**2g**)	 (**3g**)	25	66
8	 (**2h**)	 (**3h**)	After 1 minute gave a mixture of unidentifiable materials	

Table 2. Synthesis of bis-quinoxaline derivatives using EtOH/DMF.

Entry	1,2-Diamine	Product	With Tonsil		Without Tonsil	
			Time (h)	Yield (%)	Time (h)	Yield (%)
1	**2a**	**3a**	1	82	3	80
2	**2b**	**3b**	1	72	3	68
3	**2c**	**3c**	2	60	5	58
4	**2d**	**3d**	1.5	72	4	70
5	**2e**	**3e**	10	NR	10	NR
6	**2f**	**3f**	4	43	7	31
7	**2g**	**3g**	3.5	56	6	50
8	**2h**	**3h**	Unidentifiable materials			

ACKNOWLEDGEMENT

The authors thank Urmia University and Daana Pharmaceutical Co. for financial support.

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