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ORIGINAL ARTICLE

Ammonium Lauryl Sulfate: An Anionic Surfactant Catalyzed One Pot Green Synthesis of 1*H*-Benzo[*d*]imidazoles, Quinoxalines and 2,3-Dihydro-1*H*-benzo[*b*][1,4]diazepines at Room Temperature

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ABSTRACT
We have developed a greener synthetic method for the synthesis of 1H-benzo[d]imidazoles, quinoxalines and 2,3-dihydro-1H-benzo[b][1,4]diazepines from the diversity of aromatic aldehydes, 1,2-diketones and ketones respectively at room temperature using anionic surfactant, ammonium lauryl sulfate (ALS) as an efficient catalyst and water as a solvent. This protocol gave 1H-benzo[d]imidazoles, quinoxalines and 2,3-dihydro-1H-benzo[b][1,4]diazepines in good to excellent yield with high purity.
Keywords: *1H-benzo[d]imidazoles, quinoxalines, 2,3-dihydro-1H-benzo[b][1,4]diazepines, anionic surfactant, ammonium lauryl sulfate.*

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INTRODUCTION

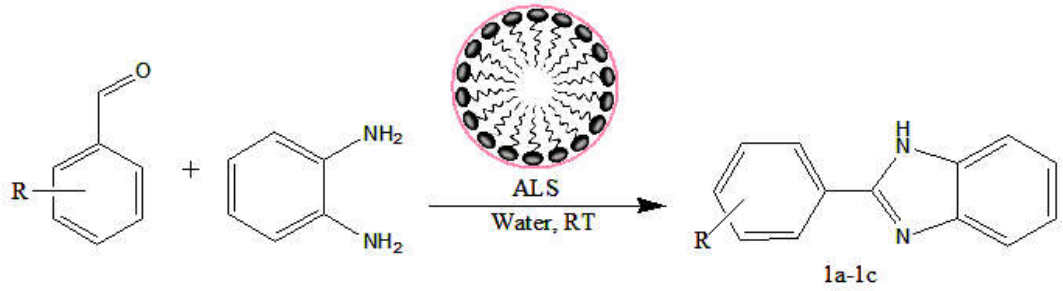
In synthetic organic chemistry, development of green methodologies in terms of solvent choice and catalyst design to reduce the waste generation is a key step in the reaction. Concept of green chemistry has open new vistas for synthetic chemists that encourage moving towards sustainable and innovative approach [1-8]. One of the important areas of green chemistry is to minimize energy consumption and replacement of toxic solvents with environmentally benign solvents. Water as a solvent has gained much attention as it is safe, inexpensive, non-toxic and environmentally friendly. Heterocycles represents significant compounds in drugs and pharmaceutically relevant substances [9]. Quinoxalines, benzodiazepines and benzimidazoles are the important class of nitrogen containing biologically active heterocyclic compounds. They are known to exhibit broad and diversified biological activities and thus, have achieved increasing interest in medicinal and pharmaceutical chemistry [10-21]. Therefore, their synthesis is desirable under the conventions of green chemistry [22]. Herein, we report a convenient and green approach for the synthesis of 1*H*-benzo[*d*]imidazoles, quinoxalines and 2,3-dihydro-1*H*-benzo[*b*][1,4]diazepines using ammonium lauryl sulfate as an efficient catalyst and water as a solvent.

MATERIALS AND METHODS

All chemicals and reagents were purchased from Hi-media and Sigma-Aldrich, and used without further purification. BRUKER AVANCE DRX-400 MHz spectrophotometer was used to record ^{1}H NMR spectra of synthesized compounds at ambient temperature using TMS as an internal standard.

General Procedure for the Synthesis of 1*H*-Benzo[*d*]imidazoles

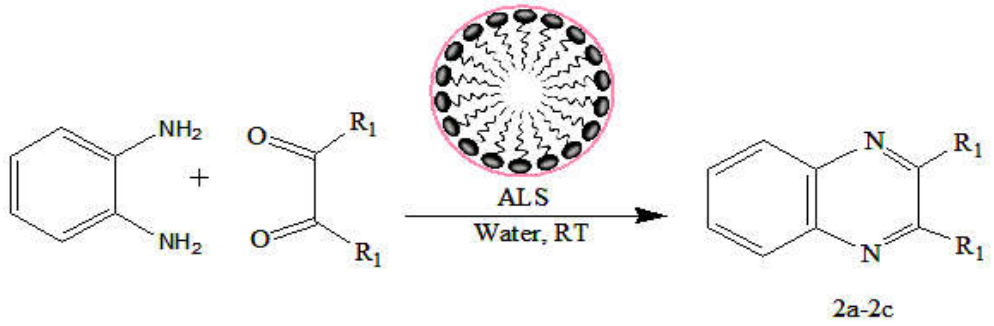
To the 100 mL round bottom flask, 2 mmol aromatic aldehyde, 2 mmol benzene-1,2-diamine and 2 mol % of 30 % ALS in 2 mL distilled water were taken and stirred on magnetic stirrer at room temperature **(Scheme 1)**. Reaction progress was monitored by silica gel TLC plates using hexane and ethyl acetate (70:30) solvent system. After completion of the reaction, crude solid product formed was washed with distilled water and dried. Recrystallization was done using ethanol.



Scheme 1. Synthesis of 1*H*-benzo[*d*]imidazoles

General Procedure for the Synthesis of Quinoxalines

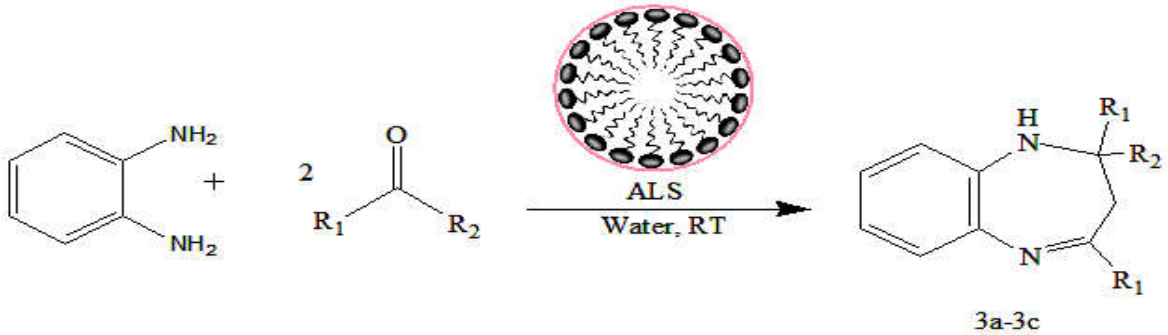
A mixture of 2 mmol benzene-1,2-diamine, 2 mmol 1,2-diketone and 2 mol % of 30 % ALS in 2 mL distilled water was taken in 100 mL round bottom flask and was stirred at room temperature **(Scheme 2).** Reaction progress was monitored by silica gel TLC plates using hexane and ethyl acetate (80:20) solvent system. After completion of the reaction, the crude solid product formed was filtered and recrystallized using ethanol: water (9:1).



Scheme 2. Synthesis of quinoxalines

General Procedure for the Synthesis of 2,3-Dihydro-1*H*-benzo[*b*][1,4]diazepines

To the 100 mL round bottom flask, a mixture of 2 mmol benzene-1,2-diamine, 4 mmol ketone and 2 mol % of 30 % ALS in 2 mL distilled water was stirred at room temperature **(Scheme 3)**. Reaction progress was monitored by silica gel TLC plates using hexane and ethyl acetate (80:20) solvent system. After completion of the reaction, reaction mixture was washed with distilled water and crude product was extracted with dichloromethane. The organic extracts were dried over anhydrous Na_2SO_4 and recrystallized using ethanol: water (9:1) to afford the pure product.



Scheme 3. Synthesis of 2,3-Dihydro-1*H*-benzo[*b*][1,4]diazepines

RESULTS AND DISCUSSION

In our present study, reaction of benzene-1,2-diamine was carried out with aromatic aldehyde, 1,2-diketone and ketones to synthesis 1*H*-benzo[*d*]imidazoles (1a-1c), quinoxalines (2a-2c) and 2,3-dihydro-1*H*-benzo[*b*][1,4]diazepines respectively using ammonium lauryl sulfate (ALS) **(Table 1)**. 2 mol% of 30% ALS effectively catalyze one pot synthesis of the above compounds in good to excellent yield at room temperature and their structures are presented in figure 1. The plausible mechanism for the formation of 1*H*-benzo[*d*]imidazoles, quinoxalines and 2,3-dihydro-1*H*-benzo[*b*][1,4]diazepines is suggested in scheme 4, 5 and 6 respectively. Ammonium lauryl sulfate is an anionic surfactant that undergoes micelle

formation in water. Its hydrophobic ends surround organic substrates, thereby inducing collisions among them, which ultimately increase the rate of the reaction. Water formed during the reaction was excluded by the hydrophilic core of the micelles, leading to the formation of the product [23].

Table 1. Synthesis of 1*H*-benzo[*d*]imidazoles (1a-1c), quinoxalines (2a-2c) and 2,3-dihydro-1*H*-benzo[*b*][1,4]diazepines (3a-3c) using 2 mol% of 30% ammonium lauryl sulfate

Entry	Product	Benzaldehyde	1,2-Diketone	Ketone	Time (min)	% Yield
1	1a	*o*-ClC_6H_4CHO	-	-	45	85
2	1b	*o*-$CH_3C_6H_4CHO$	-	-	60	79
3	1c	*p*-FC_6H_4CHO	-	-	60	82
4	2a	-	Benzil	-	90	89
5	2b	-	4,4-Dimethylbenzil	-	90	81
6	2c	-	9,10-Phenanthrenequinone	-	60	78
7	3a	-	-	Acetone	180	84
8	3b	-	-	Butan-2-one	180	86
9	3c	-	-	Acetophenone	120	82

1a: 2-(2-chlorophenyl)-1*H*-benzo[*d*]imidazole
1b: 2-*o*-tolyl-1*H*-benzo[*d*]imidazole
1c: 2-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole
2a: 2,3-diphenylquinoxaline
2b: 2,3-di*p*-tolylquinoxaline
2c: dibenzo[*a*,*c*]phenazine
3a: 2,3-dihydro-2,2,4-trimethyl-1*H*-benzo[*b*][1,4]diazepine
3b: 2,4-diethyl-2,3-dihydro-2-methyl-1*H*-benzo[*b*][1,4]diazepine
3c: 2,3-dihydro-2-methyl-2,4-diphenyl-1*H*-benzo[*b*][1,4]diazepine

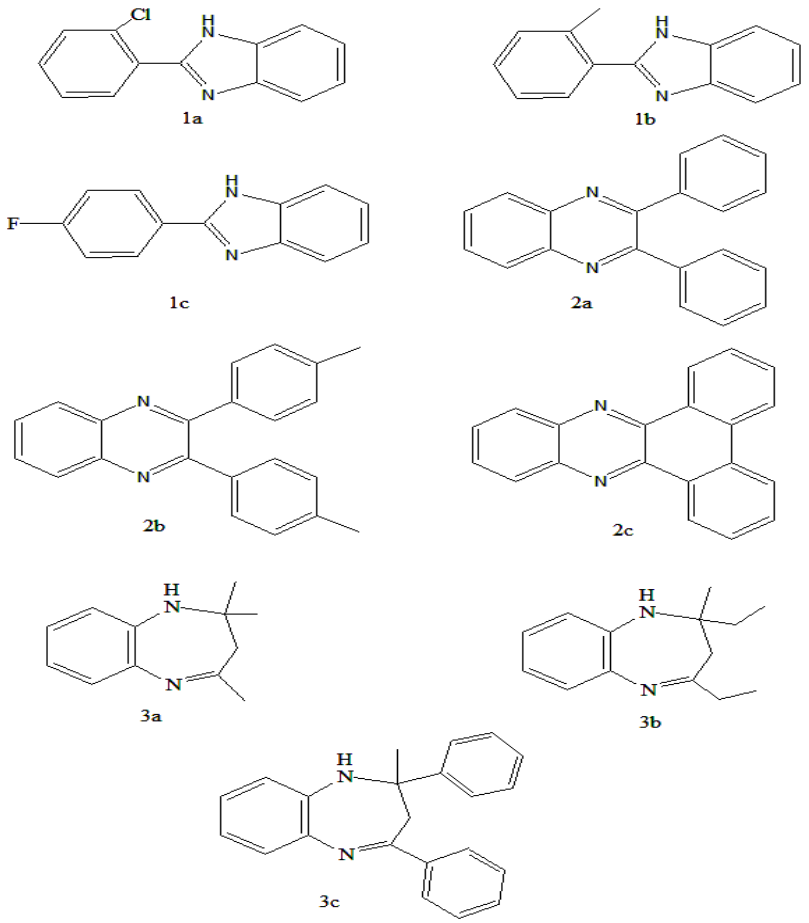
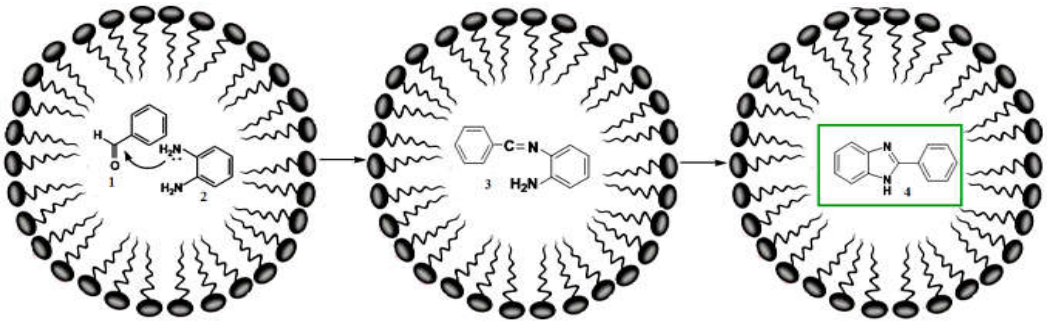
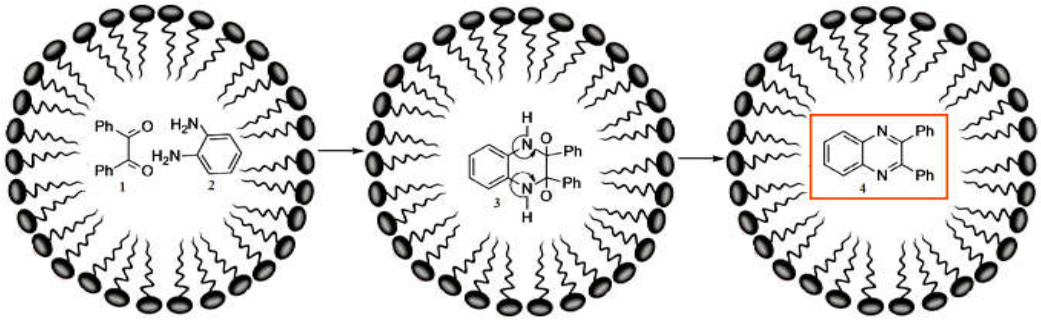


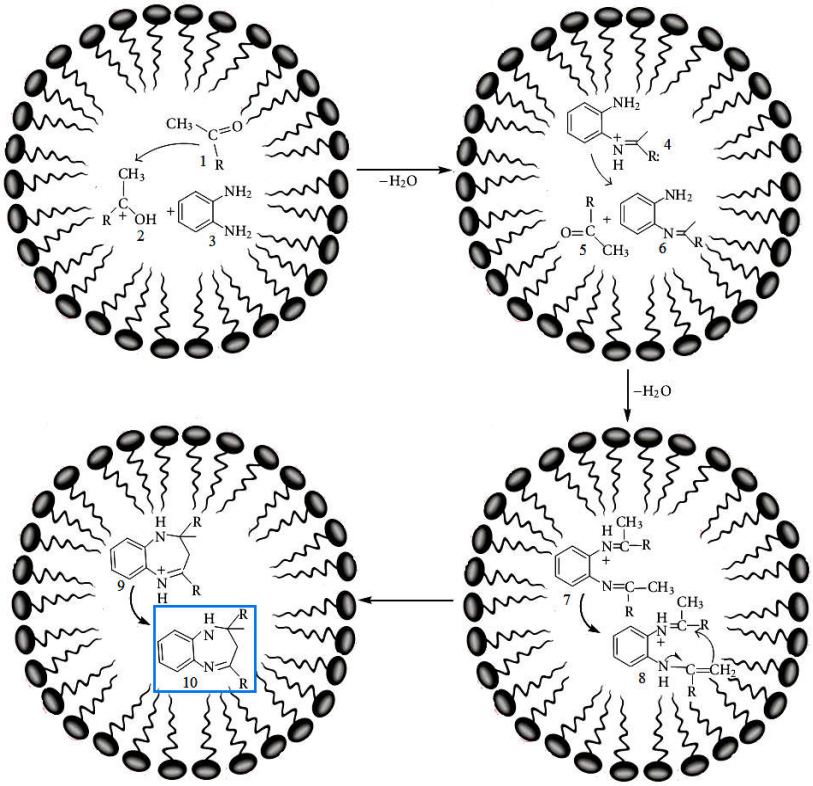
Figure 1. Structures of synthesized 1*H*-benzo[*d*]imidazoles (1a-1c), quinoxalines (2a-2c) and 2,3-dihydro-1*H*-benzo[*b*][1,4]diazepines (3a-3c)



Scheme 4. Plausible mechanism for the formation of 1*H*-benzo[*d*]imidazoles



Scheme 5. Plausible mechanism for the formation of quinoxalines



Scheme 6. Plausible mechanism for the formation of 2,3-dihydro-1*H*-benzo[*b*][1,4]diazepines

Characterization of Synthesized Compounds

Table 1, Entry 1: 2-(2-chlorophenyl)-1*H*-benzo[*d*]imidazole (1a)
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.9-7.3 (m, 4H), 7.5-8.0 (m, 4H), 8.15 (s, 1H, NH).
Table 1, Entry 2: 2-*o*-tolyl-1*H*-benzo[*d*]imidazole (1b)
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.3 (s, 3H), 6.85-7.45 (m, 4H), 7.9-8.2 (m, 4H), 8.3 (s, 1H, NH).
Table 1, Entry 3: 2-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole (1c)
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.2-7.75 (m, 4H), 8.2-8.35 (m, 4H), 8.4 (s, 1H, NH).

Table 1, Entry 4: 2,3-diphenylquinoxaline (2a)
^{1}H NMR (DMSO, 400 MHz): δ (ppm) 7.1- 7.55 (m, 10H), 7.65 -7.8 (m, 4H).
Table 1, Entry 5: 2,3-di*p*-tolylquinoxaline (2b)
^{1}H NMR (DMSO, 400 MHz): δ (ppm) 2.2 (s, 6H), 7.2- 7.6 (m, 8H), 7.7 -8.1 (m, 4H).
Table 1, Entry 6: dibenzo[*a*,*c*]phenazine (2c)
^{1}H NMR (DMSO, 400 MHz): δ (ppm) 7.4-7.85 (m, 4H), 8.2- 8.9 (m, 8H).
Table 1, Entry 7: 2,3-dihydro-2,2,4-trimethyl-1*H*-benzo[*b*][1,4]diazepine (3a)
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.2 (s, 6H), 2.35 (s, 2H), 2.6 (s, 3H), 3.25 (br, s, 1H, NH), 6.8-7.45 (m, 4H).
Table 1, Entry 8: 2,4-diethyl-2,3-dihydro-2-methyl-1*H*-benzo[*b*][1,4]diazepine (3b)
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.2 (t, 3H), 1.5 (t, 3H), 1.8 (q, 2H), 2.3 (m, 2H), 2.6 (s, 3H), 2.85 (q, 2H), 3.4 (br s, 1H, NH), 6.9-7.55 (m, 4H).
Table 1, Entry 9: 2,3-dihydro-2-methyl-2,4-diphenyl-1*H*-benzo[*b*][1,4]diazepine (3c)
^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.65 (s, 3H), 2.5 (m, 2H), 3.3 (br s, 1H, NH), 6.7-7.55 (m, 10H), 7.75-8.1 (m, 4H).

CONCLUSION

In conclusion, a simple, mild and convenient synthetic procedure has been developed for the synthesis of 1*H*-benzo[*d*]imidazoles, quinoxalines and 2,3-dihydro-1*H*-benzo[*b*][1,4]diazepines. In this method, ammonium lauryl sulfate, an anionic surfactant proved to be an efficient catalyst for the synthesis of above compounds at room temperature using water as a solvent. Method provides green synthetic approach in terms of cost effectiveness of catalyst as well as solvent, easy workup and short reaction time affording high yield of the products.

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