Synthesis and Characterization of Some New Heterocyclic Compounds Derived from Benzothiazole

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Synthesis and Characterization of Some New Heterocyclic Compounds Derived from Benzothiazole

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Abstract. The present work involves study of some new 1,3-oxazepine and diazepines derivatives by cycloaddition reaction between Schiff s bases and (Succinic imide, phthalic imide, and 3-nitophthalic) anhydride with dry benzene as a solvent. Oxazepine and diazepines derivatives from 4-chloro-6-nitrobenzo[*d*]thiazol-2-amine were synthesized. These derivatives were synthesized by the reaction of Schiff base with different anhydrides in presence of dry benzene. The starting material was 4-Chloro-6-nitro 2- aminobenzothiazole which prepared from 2-Chloro -4-nitroaniline and ammonium thiocyanate with presence of bromine and sodium acetate. The prepared compounds have been characterized by melting points and some physical properties besides the FT-IR,H-NMR spectra. The purity for these compounds was checked by TLC.
Keywords: Schiff bases, aminobenzothiazole, oxazepine and diazepines.

1. Introduction

Schiff s bases possess biological activity such as antibacterial, antifungal, antitumor, anti-HIV and herbicides [1-3]. Heterocyclic compounds are found as building units via some biological molecules [4], mostly are molecules, which have (5,7) membered ring [5-7].

The Schiff bases (SB) had been prepared by (Schiff) for the first time [8] from the condensation reaction of aldehyde or ketones with primary amines by refluxing the mixture in absolute C_2H_5OH, C_6H_6, or any other suitable solvent for one hour or few hours some times, the reaction may be catalyzed by acid [9-11]. Oxazepine, un-saturated non-homologous (7) membered heterocycle that contains oxygen in 1st position and nitrogen in 3rd position, is prepared by the pericyclic cycloaddition of Sciff bases with (Succinic imide, phthalic imide, and 3-nitophthalic) anhydrides [12]. The importance of 1,3-oxazepine is ascribed to their applications as anticonvulsant.

2. Experimental

Melting points in (^{0}C) of all the prepared compounds were recorded. FT-IR spectra had been recorded as KBr pellets, on a FT-IR BRUKER. ^{1}H-NMR spectra in DMSO solution had been recorded on the instrument BRUKER. Chemical shifts were reported as δ ppm in relation to TMS as inner standard. The progress of the reaction was observed by TLC with silica gel. Solvents had been of analytical reagent grade and of the top quality available commercially.

2.1. Preparing of 4-chloro-6-nitrobenzo[d] Thiazol-2-amine

This compound had been prepared by the means of ammonium thiocyanate with bromine and sodium acetate. The product obtained was re-crystallized from ethanol [13,14]. The structure was confirmed by FT-IR, ^{1}H-NMR and the melting point was checked. 2-chloro-4-nitro aniline was treated with CH_3COOH, then a solution ammonium thiocyanate was added to it. The thiourea compound obtained was treated with bromine. After completion of reaction, the reaction mixture was basified with liquor ammonia. A solid product of 4-chloro-6-nitrobenzo[*d*]thiazol-2-amine obtained was filtered, washed, and recrystallized.

2.2. General Method for Preparing of Schiff Bases [15-17]: The Schiff s Bases were Prepared by Reacting 2-amino-1,3-benzothiazole with Selected Aldehydes.

A solution of 4-chloro-6-nitrobenzo[*d*]thiazol-2-amine (3mmol) and appropriate substituted benzaldehyde (3mmol) in 15 ml absolute ethanol with a few drops of CH_3COOH acid was refluxed for (5-6) hrs., the

reaction was observed by TLC, and the maximum solvent had been distilled out .The mixture was cooled to room temperature afterward.
The nucleophilic addition of $–NH_2$ group of hetero to aromatic aldehydes is not so straight forward and easier due to the presence of N in heterocyclic rings [14]. All compounds were purified by re crystallization using absolute ethanol in order to avoid the hydrolysis.

2.3. Preparing of Oxazepine Derivatives [15-17]:
A mixture of the prepared Schiff base,(0.02m) and 3-nitrophthalic anhydride (0.02m) were dissolved in 15ml dry benzene with the mixture were refluxed for (3-5) hours and the excess solvent was distilled . The precipitate obtained was filtered after cooling, re crystallized in ethanol and melting points were determined.

2.4. Preparing of Diazepines Derivatives [15-17] *(4, 5): N-(4-Chloro-6-nitrrobenzo[d]thiazol-2-yl)-N-(4-(dimethylamino)benzyl)-N^4-methylsuccinamide(4), N-(4-Chloro-6-nitrrobenzo[d]thiazol-2-yl)-N-(4-(dimethylamino)benzyl)-N^4-methylphthalamide(5).*

A mixture of the prepared Schiff base (0.02m) and ((Succinic imide and phthalic imide) anhydrides (0.02m) were dissolved in 15ml dry benzene. The mixture then was refluxed for (5-6) hours . Excess solvent was distilled. The obtained precipitate was then filtered after cooled, re-crystallized by C_2H_5OH and melting points were determined.

3. Results and Discussion:
Schiff s bases are prepared through the condensation of benzothiazole with aromatic aldehyde to give the azomethine/imine compounds. The reaction is followed by disappearance of the Carbonyl group absorption band at (1690-1720) cm^{-1} with the appearanc of (C=N) absorption band at (1645 -1649) cm^{-1} (Table 1). Derivatives of oxazepine are prepared by reaction of (Succinic imide, phthalic imide, and 3-nitophthalic), anhydrides with Schiff s base derivative. It was noted disappearance of the azomethine (C=N) absorption band and appearance of the Carbonyl group absorption band at (1670-1730) cm^{-1}, and other important FTIR absorptions of compounds [18].

3.1. Characterization of 4-Chloro-N-(4(dimethylamino) Benzylidene)-6-nitrobenzo[d]thiazol-2-amine.
Compound (2) has been synthesized from the reacting of compound [1] along with 4-dimethyl amino benzaldehyde in absolute ethanol gave the imine. Condensation reaction of (equimolar quantity) of (4-chloro-6-nitrobenzo[d]thiazol-2-amine) with the 4,4 – dimethyl amino Benzaldehyde is the main technique to prepare Schiff base. The FT-IR Spectrum of compound [2] showed the appearance of (C=N) of stretching band at 1591 cm^{-1} along with (C-H) aliphatic at 2918 cm^{-1} and (C-H) aromatic at (3005) cm^{-1} and (N-H) at 3080 cm^{-1}.
^{1}H-NMR spectrum of compound (2) exhibited some signals at δ 3.08 (6H) that were assigned to 2(CH_3) protons, signals at δ 3.85 (1H) that can be assigned to (NH) protons, a signal peak at δ 9.51 (1H) that can be assigned to (N=CH) proton .There were also multiplet signals at δ 6.72-7.63 (10 H) that can be assigned to benzene ring protons.

Table 1: The IR Characteristic Bands of Compound(2).

Comp. No.	Changed part(x)	IR, KBr , υ, cm^{-1}				
		(C-H) Ar.	(C-H) Aliph.	(C=N)	(C=C)	Other Bands
2	$N(CH_3)_2$	3080	2918, 2879	1645-1649	1487, 1525	N-CH_3 1228,1246

1,3-oxazepine compound (3) was synthesized from 1,3-dipolar cycloaddition reaction of Schiff base(2) with 3-nitophthalic anhydride in dry benzene as a solvent.
The mechanism involves the addition of one σ-carbonyl to π –bond (N=C) to give 4-membered cyclic and 5-membered cyclic ring of anhydride in the same transition state [T.S]a, which opens into 3-nitrophthalic anhydride to give 7-membered ring 1,3-oxazepine(3) [19]. The FT-IR spectrum indicated band at (1695-700) cm^{-1} for lactone and (1653-1660) cm^{-1} for lactam. The FT-IR spectra identified the appearance of carbonyl groups at (1742, 1774) cm^{-1} besides the appearance of NH group at (3178) $cm^{-1.}$

Table 2: Physical Properties of the Synthesized Compounds.

Comp. No.	Molecular Formula	Molecular Weight (g/mole)	Yield (%)	M.P (^oC)	Colour	Rf
1	$C_7H_4N_3O_2SCl$	229.69	65	92-94	Yellow	0.71
2	$C_{16}H_{13}N_4O_2SCl$	360.87	67	134-137	Yellow	0.89
3	$C_{24}C_{16}N_5O_7SCl$	553.99	77	236-238	Pale yellow	0.91
4	$C_{20}H_{18}N_5O_4SCl$	459.952	55	180-182	White	0.92
5	$C_{24}H_{18}N_5O_4SCl$	508.009	59	207-209	Red	0.93

Table 3: The IR Characteristic Bands of Compounds (3-5).

Comp. No	(N-H)	IR, KBr, υ, cm^{-1}				
		(C-H) Ar.	(C-H) Aliph.	(C=O) lactam	(C=O) lactone	(C-S-C)
3	-	3050	2921,2898	1630	1732	1097
4	3109	3031	2960,2890	1670	1714	1033
5	3150	3050	2946,2890	1678	1789	1034

4. Conclusion

The research involved the preparation of a number of homogeneous ring compounds containing a derivative benzothiazole as shown in Figure 1.

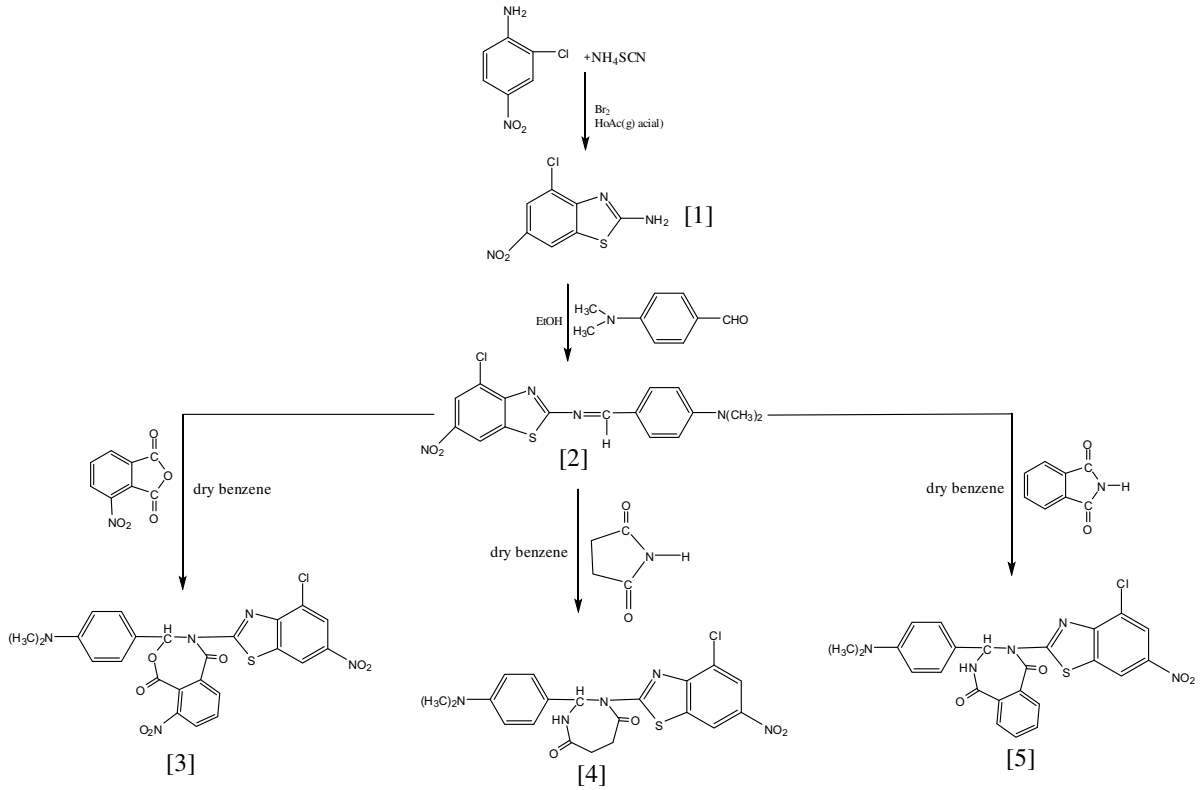

Figure 1. Homogeneous ring compounds containing a derivative benzothiazole

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