Thiadiazole Cyclic Derivatives from Aldamine Compounds (Preparation, Characterization, Thermal Stability)

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Abstract

Seven heterocyclic derivatives were synthesized by using Azotation reaction, followed by coupling reaction with phenol derivative, the resulting compound cyclized with thiosemicarbazide to yield thiadiazole derivatives which reacted with carbonyl compound (benzaldehyde) with drops of glacial acetic acid to produce imine compound followed by breaking of imine bond (CH=N) to react with (succinic anhydride, chloroaceto chloride, glycine, ortho mercapto benzoic acid) to yield cyclic derivatives from Aldamine-thiadiazole derivatives. Thiadizole-aldamine derivatives were characterized by chemical techniques such as (¹H NMR, IR and Mass-spectra, Thermal Stability).

Keywords: Therm, Technic, Stable.

Introduction

Cyclization of aldamine compounds to cyclic derivatives is highly stereo selective such as (oxazepine, lactam, azetidine, imidazole, thiazine, oxazine, diazine, ...) by reaction in two-steps by breaking of bond (CH=N) of imine group then cyclization(1-6) with dipole compound.

Cyclization reaction with imine group is an important reaction in synthetic chemistry which acts production and formation various derivative from cyclic compounds which represented in (thiadiazle, thiazine, oxazepine, thiazine, oxazane, oxazine, diazine, diazepine, thiazepine, imidazole, azetidine, ...) through condensation reaction, cyclization reaction, substitution reaction and in other fields(7-19).

Fig. 1: Cyclization of aldamine
Lactam, imidazole, oxazepine compounds have many applications in medical field, industrial field, in coordination of complexes, in reagents of pollution researches and in other applications\(^{(20-45)}\).

**Experimental Part**

Azotation reaction is used to preparation of seven new compounds by multi reactions, all these new compounds were investigated by several methods, and followed TLC papers and recrystallization by ethanol. The newly compounds were prepared through following literatures\(^{(17, 42)}\).

**Formation of Azo - Compound [1]**

Azotation reaction is used to preparation of seven new compounds by diazotation reactions through reaction of para-amino benzoic acid (0.1 mol) was dissolved in hydrochloric acid in temperature (0–5 °C), after that sodium nitrite solution was added to formation diazonium salt, the coupling compound – solution (0.1 mol) para-hydroxy benzoic acid was added to the mixture, after cooling, the product compound was filtered and washed with distilled water, dried and recrystallization from ethanol according to study\(^{(17, 42)}\) to give azo-compound [1].

**Formation of Azo – Bis (Amino Thiadiazole) Compound [2]**

The product of compound [1] (0.1 mole) refluxed with thiosemicarbazide (0.2 mole) in presence of sulphric acid (3 ml) with refluxing for (17 hrs), the resulting compound filtered, dried, and recrystallized with ethanol according to studies\(^{(17, 42)}\) to give Azo – compound [2].

**Formation of Azo-Bis Azomethine-Compound [3]**

Compound [2] (0.1 mole) refluxed with (0.2 mole) from benzaldehyde in presence of absolute ethanol with drops of glacial acetic acid for (3 hrs), after filtration, dried to produce compound involving bi azomethine groups, compound [3].

**Formation of Azo-Bis (Oxazepine) Compound [4]**

(0.1 mole) of Compound [3] was refluxed with (0.2 mole) of succinic anhydride according to papers\(^{(17, 42)}\) to give azo-Oxazepine compound [4].

**Formation of Azo – Bis (Lactam) Compound [5]**

(0.1 mole) of Compound [3] was refluxed with (0.2 mole) of chloroacetyl chloride according to papers\(^{(17, 42)}\) to give azo-lactam compound [5].

**Formation of Azo – Bis (Imidazole) Compound [6]**

(0.1 mole) of Compound [3] was refluxed with (0.2 mole) of glycine according to papers\(^{(17, 42)}\) to give azo- Imidazole compound [6].

**Formation of Azo – Bis (Thiazine) Compound [7]**

(0.1 mole) of Compound [3] was refluxed with (0.2 mole) of ortho mercaptobenzoic
acid according to papers\textsuperscript{(17, 42)} to give azo-Thiazine compound \[7\].

\[\text{Scheme 1: Preparation of Azo-hetero cycles [1 - 7]}\]

**Results and Discussion**

Azo heterocycle-Thiadiazole derivatives identified by many methods:

**The FT.IR-Investigation**

Table 1: FT-IR data (cm⁻¹) of Compounds (1-7)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Other Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>(OH)-Phenol: 3373, (N=N) Azo : (1498, 1553), (-CO-O-)Carbonyl of carboxyl group: (1701), (OH) of Carboxyl: (2665 - 3166).</td>
</tr>
<tr>
<td>(2)</td>
<td>(OH)-Phenol : 3400, (C=N) Endocycle: 1650, (N=N)-Azo: (1450, 1520), (NH) Amine: (300, 3100).</td>
</tr>
<tr>
<td>(3)</td>
<td>(OH)-Phenol : 3410, (N=N)-Azo: (1462, 1510), (CH=N) Imine: (1626), (C=N) Endocycle: 1658.</td>
</tr>
</tbody>
</table>

Fig. 3: FT-IR- Spectrum of Compound [1]

Fig. 4: FT-IR- Spectrum of Compound [2]

Fig. 5: FT-IR - Spectrum of Compound [5]
The H.NMR- Investigation

H.NMR spectra were carried out by spectrometer with solvent (DMSO-d_6). It gave several peaks at 6 DMSO-d6(solvent): 2.50, (OH) Proton of Phenol: 11.33, Protons of Aromatic ring: (7.20-7.42), (COOH) proton of Carboxylic: 12.32 in compound (1), while compound (2) appeared signals at (OH) Proton of Phenol: 11.19, Protons of Aromatic ring: (7.10-7.96), (NH_2) protons of amine: 5.07, but compound (3) gave signal at (OH) Proton of Phenol: 11.16, Protons of Aromatic ring: (7.04-7.68), (CH=N) Imine group: 8.12, while compound (4) showed peak (OH) Proton of Phenol: 11.12, Protons of Aromatic ring: (7.42-6.59), (N-CH-O) proton of Oxazepine: (3.5), (CO-CH_2-CH_2-CO-): (3.12-3.54), but compound (5) showed signal (OH) Proton of Phenol: 11.39, Protons of Aromatic ring: (7.11-7.94), (N-CH-CH-Cl) protons of azetidine: (3.01, 3.09), compound (6) showed (OH) Proton of Phenol: 11.41, Protons of Aromatic ring: (7.02-7.81), (N-CH-NH-CH_2-CO-) protons of Imidazolone: (2.89, 3.07, 4.92), compound (7) showed (OH) Proton of Phenol: 11.53, Protons of Aromatic ring: (7.23-7.71), (N-CH-S) protons of Thiazine: (3.33), and other signals in Table (2).

Table 2: H.NMR-data (6 - ppm) of Compounds (1-7)

<table>
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<td>(2)</td>
<td>DMSO-d6(solvent): 2.50, (OH) Proton of Phenol: 11.19, Protons of Aromatic ring: (7.10-7.96), (NH_2) protons of amine: 5.07.</td>
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<td>(4)</td>
<td>DMSO-d6(solvent): 2.50, (OH) Proton of Phenol: 11.12, Protons of Aromatic ring: (7.42-6.59), (N-CH-O) proton of Oxazepine: (3.5), (CO-CH_2-CH_2-CO-): (3.12-3.54).</td>
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</tr>
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</table>

Fig. 6: H.NMR – Spectrum of Compound [1]

Fig. 7: H.NMR- Spectrum of Compound [4]
Fig. 8: H.NMR- Spectrum of Compound [7]

The Mass Spectra

The results of mass spectra improved with data of mass of fragments for prepared compounds in Figures(9-11):

Fig9: Mass Spectrum of Compound (3)

Fig10: Mass Spectrum of Compound (5)

Fig11: Mass Spectrum of Compound (7)
Stability in Thermal Analysis

Other measurements were carried out for prepared compounds by thermal analysis in high temperatures, which gave high stability for (imidazole, thiazine, azetidine) cycles with azo group in structure of compounds in Figures(12 - 15).

Fig. 12: Thermal Analysis of Compound [4]

Fig. 13: Thermal Analysis of Compound [5]

Fig. 14: Thermal Analysis of Compound [6]

Fig. 15: Thermal Analysis of Compound [7]
Physical and Chemical Properties of Compounds [1 – 7]

Through the results which gave good results and good data, we found some physical properties of the seven heterocyclic thiadiazole compounds, all these data and properties appeared in Table (3).

Table 3: Some Physical and Chemical Properties for Compounds [1–7]

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Yield %</th>
<th>Kt</th>
<th>Solvents of (TLC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1]</td>
<td>68</td>
<td>0.62</td>
<td>Ethanol : Dioxan</td>
</tr>
<tr>
<td>[2]</td>
<td>74</td>
<td>0.66</td>
<td>Ethanol : Dioxan</td>
</tr>
<tr>
<td>[3]</td>
<td>70</td>
<td>0.72</td>
<td>Ethanol : Dioxan</td>
</tr>
<tr>
<td>[4]</td>
<td>70</td>
<td>0.68</td>
<td>Ethanol : Dioxan</td>
</tr>
<tr>
<td>[5]</td>
<td>72</td>
<td>0.64</td>
<td>Ethanol : Dioxan</td>
</tr>
<tr>
<td>[6]</td>
<td>68</td>
<td>0.70</td>
<td>Ethanol : Dioxan</td>
</tr>
<tr>
<td>[7]</td>
<td>64</td>
<td>0.74</td>
<td>Ethanol : Dioxan</td>
</tr>
</tbody>
</table>

References


