Synthesis of some aryl amino acetyl -2-amino-4-nitrobenzothiazole Derivatives

Khalid A. Al-Badraani

Department of Sciences Food & Biotechnology, College of Agriculture, University of Tikrit, Tikrit, Iraq

Abstract:
Substituted anilines are readily converted to 2-amino substituted benzothiazole by reaction with Potassium thio cyanate and bromine in glacial acetic acid. The 4-nitro-2-amino benzothiazole acetyl chloride obtained from reaction between 4-nitro-2-amino benzothiazole with chloro acetyl chloride. The product 4-nitro-2-amino benzothiazole acetyl chloride was allowed to react with various aryl amine to give aryl aminoacetyl 2-amino-4-nitrobenzothiazole Derivatives. The reaction of hydrazine hydrate and ethyl 3-amino beridyl acetate gave acide hydridzide. The synthesized compounds have been characterized on the basis of IR spectral analysis and the results are compatible with their assigned structures.

Introduction:
The aryl amino acetyl derivatives are used as biological activity as a potential Insecticides agricultural fungicides and localanaesthetics. 2-minoBenzothiazole are widely used as precursors for the synthesis of compounds of medicinal importance. Some of them have been showed to have antitumor activity, antituberculotic, antituberculotic, anti inflammatory and antihistamnic. Benzothiazole have also shown significant effect against cancer. Similarly acide hydridzide also shows abiological activity such as antibacterial. Thus the aim of this work was to synthesize new substituted benzothiazole with the hope that the minor portion of this moiety with amide linkage may enhance biological activity.

The scheme (1) of this work involves synthesis of different five new benzothiazole derivatives.

Experimental:
Melting point was determined on Electro thermal Apparatus were uncorrected. The IR absorption spectra were recorded by FTIR model 84005 Shimadzu Japan. Infrared spectrophotometer as KBr disk.

Synthesis of 2- Amino substituted benzothiazoles (a1-a2).

General Procedure:
To a solution of (0.1 mole) of substituted anilines and (0.4 mole) of potassium thio cyanate in 150ml of 96% acetic acid was added drop wise, with stirring 16g. (0.1 mole) of bromine dissolved in 100 ml of glacial acetic acid while the temperature was kept below (10°C). After all the bromine solution had been added the mixture was stirred for 10 hr. The combined filtered are dissolved in warm water. The combined filtrate and neutralized with 10% Na OH. The precipitate was collected on a filter and dried, recrystallization from a suitable solvent. The physical properties of the synthesized compound are given in Table (1).

Synthesis of 2-chloro acetyl amino 4-nitro benzothiazole (I) (1, 2, 3)
Freshly distilled chloro acetyl chloride (2.5ml) dissolved in dry benzene (100ml) was gradually added to (0.033 mole) 2-amino 4-nitro benzothiazole dissolved in dry Benzene (30ml). The reaction mixture was refluxed on a water bath for 2 hr. Benzene was distilled off and the residue was washed with 5% sodium bicarbonate solution to remove the acid impurities and finally washed with distilled water. It was dried and recrystallised from ethanol. Yellow powder m.p 75-78 c° yield 80%.

Synthesis of ethyl 3-amino pyridyl acetate (II). (5)
3-aminopyriden (0.02) mole was refluxed with sodium bicarbonate (0.02) mole and ethyl chloro acetate (0.02) mole for 4-6 hr. the mixture cooled & evaporated it under reduced presser. The red product is oily .yield 70%.

Synthesis of 3-amino pyridyl carboxylic acid hydrazide (III). (6)
To suspension of (II) (0.01) mole in (50) ml EtOH was hydrazine hydrate (0.05) mole added the reaction mixture was refluxed for 2hr. after cooling the product was collected and recrystallized from EtOH to give the desired product as red crystals M.P 220-222c yield 75%.
Synthesis of aryl amino acetyl-2-amo-4-nitrobenzothiazole (b1-b5). (1, 2, 3)

General procedure:
To compound (I) (0.001 mole) dissolved in 20m1, ethanol. Aryl amine (0.001 mole) was added gradually. When addition was complete reaction mixture was reflex for 6 hr. After the reaction excesses of ethanol and aryl amine were recovered distillation. The residue was washed with sodium bicarbonate to remove the acid impurities and finally with water. The product was crystallized from a suitable solvent. The physical properties of the synthesized compound are given in Table (2).

Table (1): The physical and (I.R.) spectroscopy properties to compound (A1–A2)

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>X</th>
<th>M.P. Cº</th>
<th>Yield %</th>
<th>Solv. of recy.</th>
<th>IR(KBr)cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C=\text{N}</td>
</tr>
<tr>
<td>A1</td>
<td>4-\text{NO}₂</td>
<td>108-111 (112)*</td>
<td>80</td>
<td>EtOH</td>
<td>1620</td>
</tr>
<tr>
<td>A2</td>
<td>6-\text{Br}</td>
<td>210-212 (212)*</td>
<td>85</td>
<td>ACOOH</td>
<td>1625</td>
</tr>
</tbody>
</table>

* \text{lit m.p} = 212º, 112º. (15, 16)

Table (2): The physical and (I.R.) spectroscopy properties to compound (B1–B5)

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>R</th>
<th>M.P. Cº</th>
<th>Yield %</th>
<th>Solv. Recry.</th>
<th>IR(KBr)cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>\text{\nu} C=\text{N}</td>
</tr>
<tr>
<td>B1</td>
<td></td>
<td>140-143</td>
<td>70</td>
<td>EtOH</td>
<td>1627</td>
</tr>
<tr>
<td>B2</td>
<td></td>
<td>95-98</td>
<td>40</td>
<td>EtOH</td>
<td>1627</td>
</tr>
<tr>
<td>B3</td>
<td></td>
<td>110-112</td>
<td>55</td>
<td>EtOH</td>
<td>1623</td>
</tr>
<tr>
<td>B4</td>
<td></td>
<td>104-106</td>
<td>60</td>
<td>EtOH</td>
<td>1620</td>
</tr>
<tr>
<td>B5</td>
<td></td>
<td>57-61</td>
<td>60</td>
<td>EtOH</td>
<td>1620</td>
</tr>
</tbody>
</table>
Results and Discussion:
Aniline substituted potassium thiocynate and bromine were stirring at room temp. To give the expected 2- amino substituted benzothiazole (al-a2); The structure of the synthesized compounds were confirmed by their melting point and IR spectroscopy. The characteristic absorption bands (KBr cm⁻¹) are shown in Table (1)
The -4-nitro-2-amino benzothiazole and chloro acetyl chloride were heated to give the expected 2-chloro acetyl amino (-4-nitro benzothiazol). The IR spectrum of this compound -2-chloro acetyl amino -4-nitro benzothiazole is showed a band at 1712 cm⁻¹ which was assigned to The typical carbonyl group for acid chloride. More over this compound exhibited significant bands in the region at (3080, 1450) belong to C-H arm., C=N, respectively that clearly indicated the presence of benzothiazole. The 3-amino pyridyl acid hydrazid was synthesized from 3-amino pyridyl acetate and hydrazine hydrate as it was stated in the experimental part. the IR –spectrum of this compound showed (KBr cm⁻¹ ) stretching bands at (3300 , 3190 and 3041 ) cm⁻¹ which assigned to the asymmetrical and symmetrical band stretch bands of NH2 and ( NH ) group and band at 1720 cm⁻¹ which was assigned to the carbolyn group for acid hydridiz . a number of N-aryl –N-2-acetyl( -4-nitro benzothiazol ) ( B1-B5 ) were synthesized through the reaction of compound 2-chloro acetyl amino–4-nitro benzothiazol with aryl amines in the presence of ethanol ( scheme 1 ).The structure of the synthesized compounds were confirmed by their melting point and IR-spectroscopy . The characteristic absorption bands (KBr cm⁻¹) are shown in Table (2). It was worth to say here that the synthesized compounds will be studied in the nearest future to show their expected biological activity.

Reference:
16- Khsrow zamani, khallil faghahi (2003) " synthesis of some new substituted 1, 2, 4 – triazole & 1, 3, 4- thidiazole & their derivatives “. Turk. J. chem. Soc. 27, 119-125
تحضير بعض مشتقات أريل أمينو-استيل-4-مينو-بزوثنبازارول
خالد عبد العزيز عطية البد راني
قسم علوم الأغذية والتقانات الإحيائية، كلية الزراعة، جامعة تكريت، تكريت، جمهورية العراق

الملخص:
يتضمن البحث تحضير عدد من مشتقات أريل أمينو-استيل-4-مينو-بزوثنبازارول (b1-b5) من خلال مفاعلة معيّنة معيّنة مع أمينات أريلية مختلفة، وكذلك تم الحصول على الهيدراز س [III] من خلال مدير معيّنة معيّنة مع الهيدرازين المائي، وتم تشخيص المركبات الناتجة [II] بالطرق الفيزيائية والطيوفية المتاحة وقد دلت النتائج المستحصلة على صحة التراكيب المفترضة.