

Synthesis of sulphur-containing heterocyclic compounds By reaction derivatives of chloroacetamido with sodium sulphide

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Abstract

Synthesis of 1,2,4,5-bis(cyclo)tetra(acetamido)sulphidebenzene and 1,2-cyclo diacetamidossulphide-4,5-dinitrobenzene from the reaction of 1,2,4,5-tetra(chloroacetamido)benzene and 1,2-dichloroacetamido4,5dinitrobenzene with hydrous sodium sulphide ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$). The structures were confirmed by the use of I.R., $^1\text{H-N.M.R}$ spectroscopy

Introduction

During the last decades there have been continuous and intense studies on the chemistry of heterocyclic sulphur containing compounds. The important of these compound arises from their use as starting material for the synthesis of polymer and their possible biological implication reported by (Yue, McDonald, Richard, Dittmer, Zoller, Block).

Mukherjee and et.al synthesis Benzo[b] thiophene synthesis from tertiary benzamide, uses as starting material readily available *N,N*-diethyl benzamid carrying different substituents in the benzene ring, reported a novel synthesis of 7-hydroxy benzo[b] thiophene starting from commercially available thiophene-2- carboxylic acid by Samanta and application of directed metalation in ring annulation leading to poly condensed sulfur heterocycles annulation of six-membered oxygen sulfur heterocycles was reported also reported by Mukherjee and et.al and construction of five-membered heterocyclic compounds via radical cyclization study by Berlin Benzo and pyrido thiazepines have attracted considerable attention because of their remarkable diversity of biological activities. As structural analogues of benzazepines and diazepines they show wide range of pharmacological properties study by Dolling Cyclo condensation of 3-(*N*-methyl acetamido)-2-chloro pyridine gives *N*-methyl-2-aryl pyrido [2,3-b][1,5]thiazepin-4(5H) ones .The synthesis and reaction of 4H-1,3,4-benzothiadiazine pyridothiadiazine and 1,2,4triazinothiadiazine have been of recent interest of a number of research groups including our own reports by

[Couture, Vukov, Elliott, Neunhoffer and Heravi] Cyclic mono sulphide diamide N,N ethylene thiodiacetoamide was prepared in good yield by Hussain. Fayadh found that reaction of ethylene diamine with methyl or butyl dithiodiglycollate afforded cyclic disulphide diamide compound in excellent yield. Reaction of *vic*-alkynylchloro- and *vic*-chloro-(1-oxoalk-2-ynyl)-anthraquinones with Na₂S in ethanol has been shown to afford anthrathiophenediones and anthrathiopyrantriones, respectively, generally in good yield reported by Mark. Also some cyclic Nine-membered ring contains sulfur atom has been synthesized by Hussain and Abdule.

Experimental:

Melting points were determined with electro thermal melting point apparatus. Infrared spectra were recorded by using Unicam Model Sp3-300S spectrometer. The proton nuclear magnetic resonance were obtained using Variant, Bruker, 300MHz.

1- 1,2 diamino 4,5- dinitro benzene(2)

5ml of H₂SO₄ and 5ml of HNO₃ was placed in ice-bath (2gm) of o-phenylene diamine was added to a mixed acid. with shaking and cooling, (2.5gm) of ice was added until the precipitate was formed. The precipitate was filtered, and recrystallized from water and dried in vacuum desiccator over CaCl₂, yielding the product as a pink solid (3.5gm, 87%) m.p = (120-121)C^o

2- 1,2,4,5- tetra aminobenzene (3):

(2)gm of 1,2- (diamino) 4,5-(dinitro) benzene, was added to (9)gm of tin in (20)ml of HCl was heated under reflux for (25min) after cooling 10% NaOH was added until the white solid obtained (0.8 gm, 47%) m.p = (230C^o) dec.

3- 1,2 -dichloroacetamido - 4,5-dinitrobenzene (4):

A solution of 1,2-diamino -4,5-dinitrobenzene (0.396 gm, 0.002 mole) in ethanol (6 ml, 99%) was added to a solution of ethyl chloroacetate (0.49 gm, 0.43 ml, 0.004 mole) and the mixture was heated under reflux for 3h. after cooling the brown precipitate was formed. The precipitate was filtered and washed with water, dried in vacuum desiccator over CaCl₂, yielding a brown solid (0.4 gm, 69%) m.p = (210C^o) dec.

4- 1,2,4,5 -tetra (chloroacetamido) benzene (5):

A solution of 1,2,4,5-tetraaminobenzene (0.425 gm, 0.002 mole) in ethanol (6 ml, 99%) was added to a solution of ethyl chloroacetate (1.225gm, 1.074ml, 0.0025 mole) the mixture was heated under reflux for (5h.) a gray solid obtained (0.2 gm, 20%) m.p = (350C^o) dec.

5- 1,2- cyclodiacetamidodisulphide-4,5-dinitrobenzene (6):

To a stirred hot solution (70-80)C^o of 1,2-dichloroacetamido-4,5-dinitrobenzene (0.57 gm, 0.002 mole) in ethanol (13.5ml) was added a solution of Na₂S.9H₂O (0.48 gm,

0.002 mole) in distilled water (4ml). The mixture was heating with stirring till a gray precipitate formed a gray solid was collected (0.2 gm, 40%) m.p = 235C° dec.,

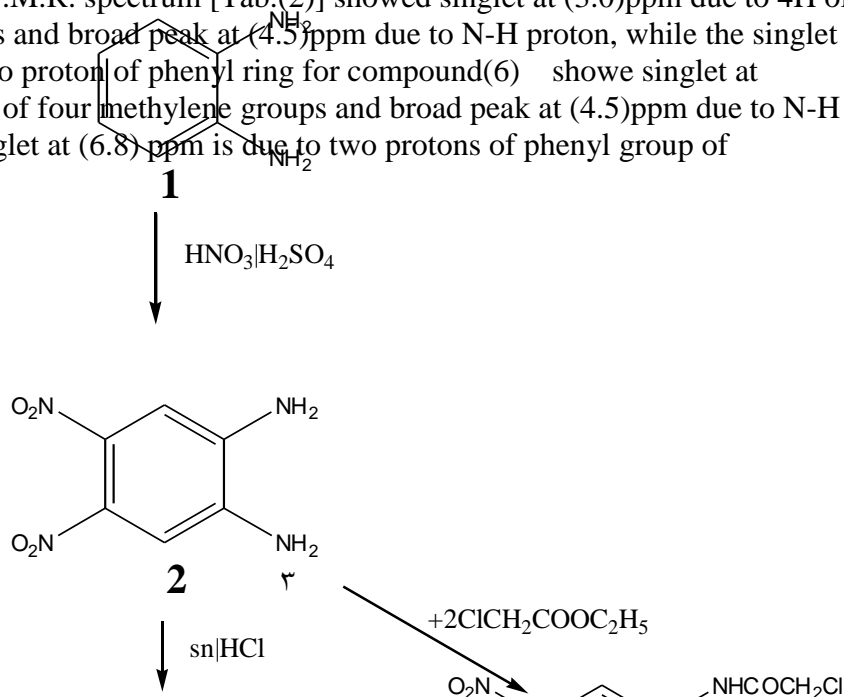
6- 1,2,4,5 –bis-cyclotetra(acetamido)sulphidebenzene (7):

To a stirred hot solution (70-80)C° of 1,2,4,5- tetra(chloroacetamido)benzene (0.1gm, 0.000225 mole) in ethanol (5ml) a solution of Na₂S.9H₂O(0.2g) in a water (2ml) was added the white product formed (0.05gm, 62.5%) m.p= 360C° dec.

Results and Discussion:

1,2- diamino 4,5-dinitro benzene(2) was synthesized from nitration of 1,2(diamino) benzene(1). The I.R. spectrum [Tab.(1)] showed bands at 1500 and 1300cm⁻¹ due to assymmetric and symmetric NO₂ groups but remaining the two peaks at (3300-3400cm⁻¹) due to primary amine. The ¹H-N.M.R. spectrum[Tab.(2)] showe a broad singlet at (3.2) ppm for four protons of NH₂ and singlet at (6.7) ppm to two protons of phenyl group . Therefore according to spectral studies the product could be assigned as 1,2-diamino 4,5-dinitro benzene(2). The reduction of compound (2) by tin (Sn/HCl) lead to the compound (3). The I.R. spectrum [Tab.(1)]. Showed the bandes at (1500-1300cm⁻¹) have been disappiare bands at (3300 - 3400 cm⁻¹) that due to primary amine. The ¹H-N.M.R. spectrum [Tab.(2)] showed. Singlet at (3.2) ppm for eight protons of amino groups with singlet peak at (6.8)ppm. due two protons of aromatic ring. The reaction of compounds (2), (3) with ethyl chloroacetate leads to formation of compounds (4), (5). The I.R. spectrum[Tab.(1)] showed band at 3300 , 1560 cm⁻¹and 3300,1580due to N-H stretching and bending for compound(4),(5) indicating that primary amine converted to secondary amine. Whilst a second band at 1670 cm⁻¹in each compounds could be atributed to carbonyl group of the secondary amides these frequency are due to the meseomeric effects in amides and band at750cm⁻¹for C-Cl. The ¹H-N.M.R. spectrum[Tab.(2)] for compound (4) showed singlet at (3.0)ppm due to four methylene protons with broad singlet at (4.5)ppm due to N-H protons , and showed singlet at (3.7) ppm for eight protons of four methylene group with broad singlet at (4.5)ppm to one of N-H group, while singlet peak at (6.8) ppm due to two protons of phenyl group of compound(5).

The reaction of compounds (4), (5) with Na₂S.9H₂O leads to formation of cyclic compounds (6),(7). The I.R. spectrum [Tab.(1)] showed strong absorption band at 1670cm⁻¹ for C=O stretching of secondary amide, and the absorption peak for C-Cl were disappeared and a new band appeared at 650cm⁻¹ for C-S stretching in each two compounds.The ¹H-N.M.R. spectrum [Tab.(2)] showed singlet at (3.0)ppm due to 4H of two methylene groups and broad peak at (4.5)ppm due to N-H proton, while the singlet at (6.7)ppm due to two proton of phenyl ring for compound(6) showe singlet at (3.7)ppm due to 8(H) of four methylene groups and broad peak at (4.5)ppm due to N-H proton. While the singlet at (6.8) ppm is due to two protons of phenyl group of compound(7).



Scheme(1)

Table(1):The I.R.data for prepared compounds.

compound	NO ₂	NH _{str.}	NH _{bend.}	C=O	C-Cl
2	1500-1300	3300-3400	1560	-----	-----
3	-----	3300-3400	1560	-----	-----
4	1500-1300	3300	1580	1670	750
5	-----	3300	1560	1670	750
6	1500-1300	3300	1580	1670	-----
7	-----	3300	1560	1670	-----

Table (2):The ¹H.N.M.R.for the prepared compounds.

<i>Compound</i>	<i>δPPm</i>	<i>Intensity</i>	<i>Multiplicity</i>	<i>Assignment</i>
2	3.2 6.7	2 1	<i>b</i> <i>s</i>	<i>NH₂-proton</i> 2H-aromatic proton
3	3.2 6.8	4 1	<i>b</i> <i>s</i>	<i>NH₂-proton</i> 2H-aromatic protons
4	3.0 4.5 6.7	2 1 1	<i>s</i> <i>b</i> <i>s</i>	<i>CH₂ of two methylene groups</i> N-H proton 2-H aromatic protons
5	3.7 4.5 6.8	4 2 1	<i>s</i> <i>b</i> <i>s</i>	<i>CH₂ of four methylene groups</i> N-H proton 2H-aromatic protons
6	3.0 4.5 6.7	2 1 1	<i>s</i> <i>b</i> <i>s</i>	<i>CH₂ of two methylene groups</i> N-H proton 2-H aromatic protons
7	3.7 4.5 6.8	4 2 1	<i>s</i> <i>b</i> <i>s</i>	<i>CH₂ of four methylene groups</i> N-H proton 2-H aromatic protons

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تحضير مركبات غير متجانسة تحتوي على كبريت

من تفاعل مشتقات كلورو اسيتاميد مع كبريتيد الصوديوم

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الخلاصة

في هذا البحث تم تحضير مركب ١، ٢، ٥، ٤ ثنائي حلقة رباعي اسيتاميد بنزين من تفاعل ١، ٢، ٤، ٥ رباعي اسيتاميد كبريتيد بنزين ومركب ١، ٢، ٤، ٥ ثنائي حلقة اسيتاميد ٤، ٥ ثنائي نايثرو بنزين من تفاعل ١، ٢، ٤، ٥ رباعي (كلورو اسيتاميد) بنزين و كلورو ١، ٢ ثنائي اسيتاميد ٤، ٥ ثنائي نايثرو بنزين مع كبريتيد الصوديوم المائي $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ و تم تشخيص المركبات باستخدام طيف الاشعة تحت الحمراء و الرنين النووي المغناطيس.