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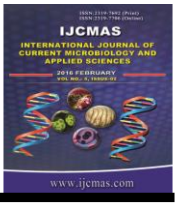

Original Research Article

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Synthesis and Study of New N-Aryl Pyrroles

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ABSTRACT

Some new N-aryl–2,4-dimethyl pyrroles which widely used to prepared an insecticide were synthesized through splitting of SO_2 – group from the corresponding sultams through heating in the presence of copper metal. The products were diagnosed by using UV, NMR spectrum, infrared (IR) in Bangor university - wales – UK, moreover to diagnosed the physical properties for preparing compounds.

Keywords

Pyrrole,
Sultone, Sultam

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Introduction

Although sultone (aliphatic or aromatic) have long history in chemical synthesis works. They are widely investigated because of their important roles that play in various types of dyes, chemical intermediate in the production of fungicides, cation- exchange resins, detergents, as a corrosion inhibitor for metal.[1,2,3a] .

Moreover, sultone and aryl-pyrroles derivatives, were used to prepared an insecticide which is a substance used to kill insects. Insecticides are used in agriculture, medicine, industry and by consumers. Insecticides are claimed to be a major factor behind the increase in agricultural 20th century's productivity. [3b] the synthesis of first series of (1,8-naphtho sultone) was reported by Erdmann [4] a number of mono and bithaizine sultams have been known [5,6,7].

These compounds were prepared from aromatic primary amines and sultones. Morel and Verkad prepare some furans from the corresponding sultones under the influence of heat in the presence of copper powder as heat conductor. [8] Using identical conditions, Helferich and Co-workers were able to synthesis (2,4-dimethyl pyrroles) from the corresponding (N-aryl-2,4-dimethyl butadiene-1,3-sultones) using copper or lead oxide. [9,10] In this work many new pyrroles were synthesized and the structures of the products characterized using (UV, I.R., NMR) and physical constants

Experimental

Synthesis of (2,4-Dimethyl Butadiene -1,4-Sultone)[11-13]

Conc. sulfuric acid (5.6 ml, 0.1 mol) was gradually added at 0 °C to a stirred mixture of acetic anhydride (20.4 ml, 0.2 mole) and mesityl oxide (11.0 ml, 0.1 mol). The reaction mixture was stirred for 2 hrs at 0 °C, then left overnight in the fridge. After that the mixture was stirred for 24 hrs at room temperature, followed by the addition of water (100 ml) to give a precipitate which was filtered, and recrystallized from methanol to give) (19.8 g, 90 %).

Synthesis of Compounds (1, 2, and 3)

A mixture of (2,4-dimethyl butadiene–1,4-sultone) (3.2 g, 0.02 mole) and *m*-phenylene diamine, *o*-phenylene diamine and benzidine alternatively, was heated on oil bath at (140 - 170 ºc), till the completion of the reaction then dilute HCL was added after cooling of the mixture, the reaction mixture was poured on dimethyleformamide (DMF) (4.0 ml), the products was precipitated on cooling and then filtered, (table 1) .

Synthesis of N-aryl 2,4-Dimethyl Pyrroles : (4 , 5 and 6)

A mixture of (0.001 mol) of compounds (1,2 and 3) and (5 g) of copper powder were placed in distillation flask, the mixture was heated in an oil bath to 220 ºc, SO_2 gas bubbles were liberated from the reaction vessel. after finishing of the bubbles (3 hrs), the reaction mixture was cooled and (25 ml) of ether was added, treated with 10% solution of Na_2CO_3, the organic layer separated and washed with water several times, the solvent evaporated and a pure liquids was obtained, (table 2).

Results and Discussion

The synthesis of (2,4-dimethyl butadiene-1,4-Sultone) was according to the method described by Morel and Verkade [9] from the reaction of mesityl oxide and acetic anhydride, the yield was 90 % with melting point (71 ºc), yellow crystal, the I.R. spectra has a characteristic bond at (1160 – 1315 cm^{-1}) for the SO_2 group of the sultone ring, a band at (2830 – 2980 cm^{-1}) for the C-H stretching of the two methyl groups, the conjugated diene system appeared at (1490 cm^{-1} and 1590 cm^{-1}) .

Synthesis of Sultams

Sultams are an important compounds, they act as sulfonylating agents of serine enzymes, inactivating the enzyme by forming a stable adduct.[14,15] A number of bithiazinesultams have been prepared from reaction between aromatic primary amines and sultone.

In this paper two moles of (2,4-dimethyl butadiene-1,4-sultone) treated with one mole *m*-phenylene diamine, *o*-phenylene diamine and benzidine giving the products 2,2'-(1,3-phenylene)bis(3,5-dimethyl-2H-1,2-thiazine 1,1-dioxide) compound (1); 2,2'-(1,2-phenylene)bis(3,5-dimethyl-2H-1,2-thiazine 1,1-dioxide) compound (2); and 2,2'-([1,1'-biphenyl]-4,4'-diyl)bis(3,5-dimethyl-2H-1,2-thiazine-1,1-dioxide) compound (3); respectively as in scheme (I) .

Table.1 Physical Data of Compound (1 , 2 And 3)

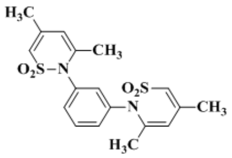
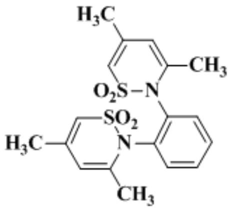
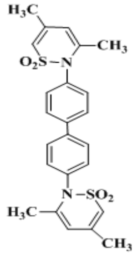
Compound NO.	Yield %	Melting point ºC
1	72.6	215 - 217
2	61.9	207 - 209
3	44.0	250 - 202

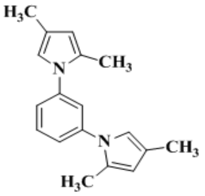
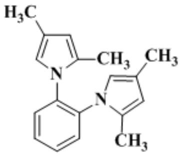
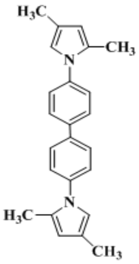
Table.2 Physical Data of Compound (4, 5 And 6)

Compound NO.	Yield %	Boiling point (10 mm Hg)
4	64	93 - 95
5	69	82 - 85
6	74	112 - 116

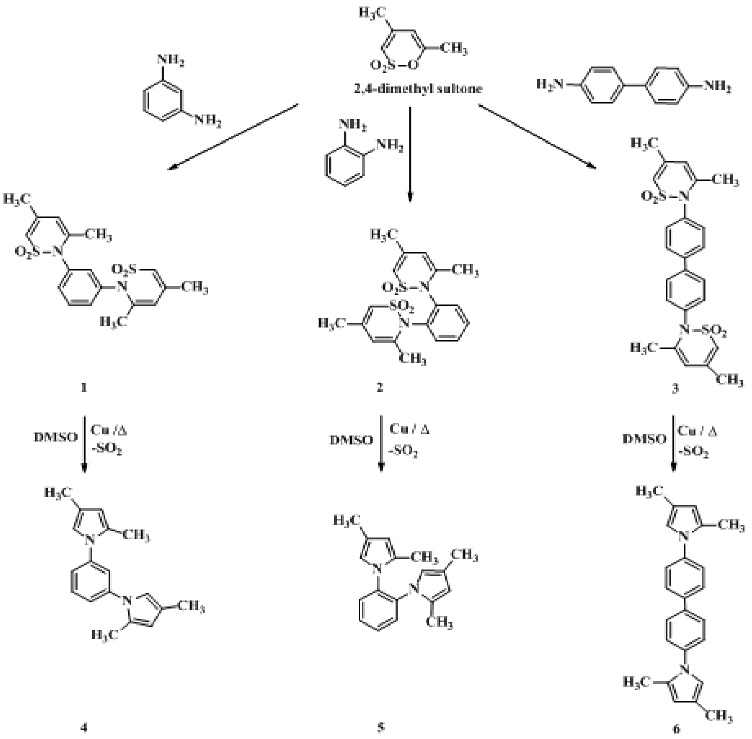
Fig.1 Preparation of (2,4-Dimethyl Butadiene-1,4-Sultone)

Table.3 Nmr Data for Compounds (1 - 6) Respectively

compound	^{1}HNMR (500 MHz, $CDCl_3$)	^{13}CNMR (400 MHz, $CDCl_3$)
 (1)	δ 6.36 (br d, J = 1.4 Hz, 1H), 6.35 (br d, J = 1.4 Hz, 1H), 6.29 (d, J = 0.9 Hz, 2H), 6.25 (t, J = 1.5 Hz, 1H), 5.82 (d, J = 1.0 Hz, 2H), 2.43 – 2.15 (m, 7H), 2.10 – 1.89 (m, 7H).	δ 144.99, 141.58, 134.37, 132.10, 130.79, 129.71, 116.03, 111.00, 20.86, 18.69.
 (2)	δ 6.80 – 6.70 (br m, 1H), 6.60 – 6.50 (m, 1H), 6.22 (d, J = 0.9 Hz, 1H), 5.73 (d, J = 1.0 Hz, 1H), 2.25 (br d, J = 0.9 Hz, 3H), 1.92 (br d, J = 0.6 Hz, 3H).	δ 145.00, 139.62, 138.47, 129.69, 129.02, 116.04, 110.35, 20.87, 18.70.
 (3)	δ 7.51 (br d, J = 7.5 Hz, 4H), 6.81 (br d, J = 7.5 Hz, 4H), 6.27 (d, J = 0.9 Hz, 2H), 5.89 (br d, J = 0.6 Hz, 2H), 2.27 (m,6H), 1.97 (m, 6H).	δ 145.06, 141.65, 137.32, 136.99, 129.56, 129.22, 116.10, 111.07, 20.93, 18.76.

 (4)	δ 7.74 (br t, J = 1.4 Hz, 2H), 7.54 (dd, J = 8.0, 6.9 Hz, 2H), 6.98 – 6.77 (m, 2H), 6.11– 5.8 (m, 2H), 2.20 – 2.11 (br m, 6H), 1.95 – 1.66 (m, 6H).	δ 141.60, 128.70, 127.24, 126.32, 123.33, 117.79, 116.04, 114.50, 11.98, 11.51.
(5) 	δ7.50 - 7.31 (br m, 4H), 6.42 – 6.38 (m, 2H), 5.98 – 5.94 (m, 2H), 2.17 – 2.13 (m, 6H), 2.03 – 1.99 (m, 6H).	δ 131.77, 128.43, 128.04, 126.41, 124.90, 118.00, 115.11, 11.42, 10.95.
 (6)	δ 7.81 – 7.65(br t, J = 1.3 Hz, 4H), 7.67 – 7.55 (m, 4H), 6.44 – 6.42 (m, 2H), 6.06 – 6.01 (br m, 2H), 2.18 – 2.11 (m, 6H), 2.04 – 1.98 (m, 6H).	δ 137.00, 134.79, 128.03, 127.26, 125.65, 123.59, 117.12, 115.37, 11.31, 10.84.

Scheme.1 Synthesis of Compounds (1 to 6)



The I.R. spectra of the products were nearly identical. The characteristic absorption bands of the SO_2 group was shifted to a higher frequencies it self (1160–1315 cm^{-1}), and anew band at (3050 cm^{-1}) corresponds to (C-H) stretching of aromatic rings, and a band at 1140 cm^{-1} for C-N) bond stretching.

Synthesis of N-aryl Pyrroles

Helferich and co-workers [6,10] were able to synthesize (2,4-dimethyl pyrroles) from the corresponding (N-aryl-2,4-dimethyl butadiene-1,4-sultam) Using copper lead oxide as heat conductors. In this work a number of new pyrroles were synthesized from the heating of compound (1), (2) and (3) in the presence of copper using DMSO as reaction medium, the heating is continued until the splitting of SO_2 was diminished, giving compounds (4, 5 and 6). The U.V. spectrum of N-aryl pyrroles shows absorption maximum in the range of (202 - 208 nm) for the pyrrole ring and another absorption peak at (238 - 241 nm) for N-aryl ring. the obtained results are in good agreement with those pyrroles of nearly similar structure in the I.R. spectrum of the obtained pyrrols , the characteristic bands for SO_2 group of the sultam ring (1160 and 1315 cm^{-1}) are completely disappeared, indicating the splitting of the SO_2 group of the sultam and conversion to pyrooles. the other absorption bands are observed at their expected positions, for the aromatic C-H stretching at (3025 cm^{-1}), for the two methyl groups attached to the pyrrole ring at (2850 – 2980 cm^{-1}) and for the conjugated diene system at (1490 and 1590 cm^{-1}), while the N-C stretching appeared at 1140 cm^{-1} .

* Noticing

Scheme (I) we found that sultams (1, 2 and 3) give the pyrroles (4, 5 and 6) respectively.

In conclusion, the proposed experimental techniques that have been used in current studies are quite simple. The importance of the present investigation is to demonstrate the possibility of using a method depend on removable of SO_2 – group from the corresponding sultams through heating in the presence of copper metal to synthesized several of new N-aryl–2,4-dimethyl pyrroles.

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