REACTION OF 4-BENZYLIDENE-2-PHENYLOXAZOL-5(4H)-ONE WITH 3,4-DITHIO-TOLUENE IN THE PRESECE OF TRIETHYLAMINE.

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ABSTRACT

Unsaturated oxazol-5(4H)-ones constitute an important class of synthon. In this paper we present our findings on the reaction of 4-benzylidene-2-phenyloxazol-5(4H)-one and 4-cyclohexylidene-2-phenyloxazol-5(4H)-one and 4-cyclohexylidene-2-phenyloxazol-5(4H)-one with 3,4-dithio-toluene in the presence of triethylamine. The intermediates can be isolated under nautral conditions. Base mediated reaction of 3,4-dithio toluene with 4-benzylidene-2-phenyloxazol-5(4H)-one in boiling benzene was unsuccessful but simple heating of these reactants at an elevated temperature give 2-benzamido-2-cyclohexyl-7-methyl-1,4-benzodithian-3-one.

Keywords: Benzodithian-3-one by oxazolone

INTRODUCTION

Oxazolones and their derivatives are the compounds which are used in synthesis of insecticides and drugs, e.g. D-penicilamine, levoutiroxin, etc. although these compounds have fluoresccense properties [1-4]., and also they are used as a selective electrode for metals specially heavy metals as carrier ion [5-7].

In order to study the reaction of 2-phenyl-5(4H)-oxazolone and 4-bezylidene-2-phenyl-5(4H)-oxazolone with 3,4-dithio-toluene in the presence of triethylamine as lewis base have now been investigated. When a mixture of 3,4-dithio-toluene and 5(4H) oxazolone derivatives, triethylamine mediated mixed throughly gives product. It is noteworthy that product react with bromine-water, therefore the olefinic bond is present in the product. It seems that 3,4-dithio-toluene reacts as a nucleophile with oxazolones and turns brought about by cleavage of the 1,5-bond of the oxazol-5(4H)-one ring. On the other hand when mixture of oxazolones derivatives and 3,4-dithio-toluene in the presence of triethylamine was heated in elevated temperature gives new product that does not react with bromine-water and the compound, believed to be 2-benzamido-2-cyclohexyl-7-methyl-1,4-benzodithian-3-one. The product reported were characterized by spectral data and elemental analysis.

RESULTS AND DISCUSSION

When 2-phenyl-5(4H)-oxazolone or 4-benzylidene-2-phenyl-5(4H)-oxazolone or 4-

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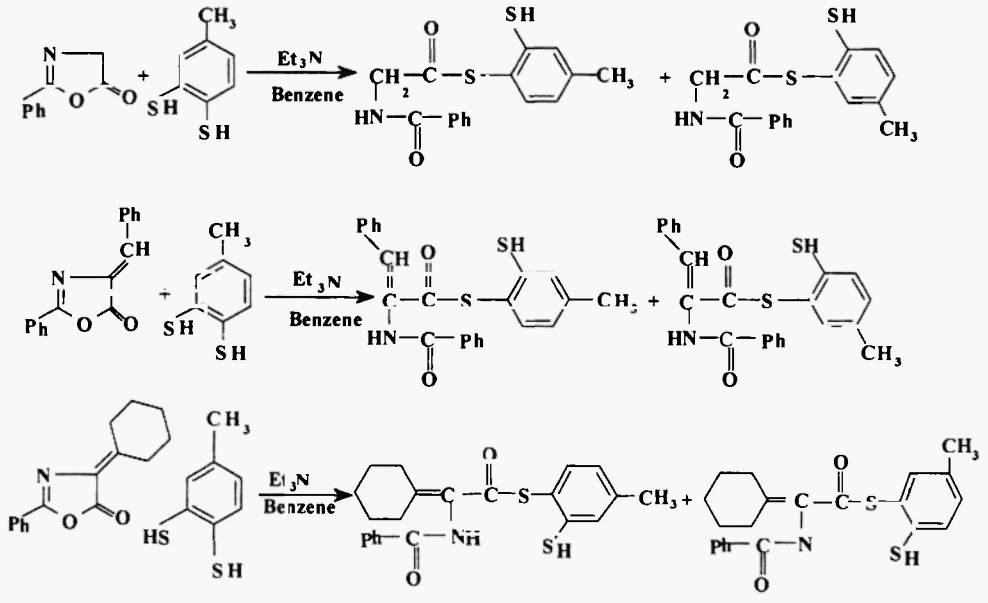
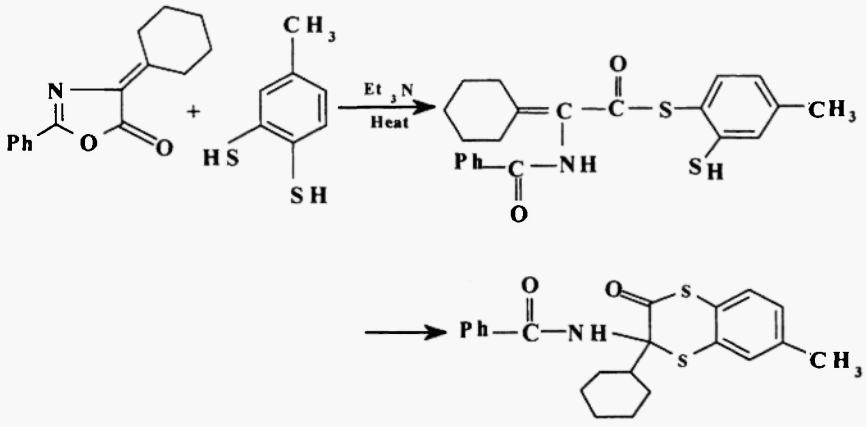
cyclohexyliden-2-phenyl-5(4H)-oxazolone mixed with 3,4-dithio-toluene in the present of triethylamine at room temperature, within a few minutes, it gives product. It seems that 3,4-dithio-toluene reacts as nucleophilic reagent to carbonyl group of oxazolone ring, and ring cleavage have been occurred. It should be remember that both thio groups are able to attact carbonyl group (ortho and para), therefore we haveisomeric products, but as we know that the group of para is more reactive than the meta. Therefore one of these isomers is major product.

Althogh these isomeric products could not be separated with ordinary methods nevertheless they were determined with capillary electrophoresis[10].

Also if 4-benzylidin-2-Phenyl-5(4H)-oxazolone mixed with 3,4-dithio-toluene in the present of triethylamine at 120-130°C in this condition, the ring of oxazolone cleaves, and undergoing intramoleculary addition reaction which produces the desired compound.





EXPRIMENTAL

Preparation of 2-phenyl-5-(4H)oxazolone.[11]

Hippuric acid (20g). and acetic anhydride (130ml) were heated on a water bath for 20 min, with frequent shaking, then poured into benzene (200ml), after that added ice water (200 ml), and stirred for 30 min, then the benzene layer was stirred with 1% sodium hydrogen carbonate solution (2L), untill acetic acid had been removed and then washed, with cold water, after that the benzene was removed below 40°C under vaccum. The resulting solid on recrystallization from benzene gave yellow plates (10 gr) 83-84°C m.p.

Preparation of (2-mercapto-4-methyl-phenyl)-2-Benzamido-thioethanoat and (2-mercapto-5-methyl-phenyl)-2-Benzamido-thioethanoat.

To a solution of (0.322gr, 2mmol) of 2-phenyl-5-(4H)oxazolone in 20 ml of dry benzene were added (0.312ml, 2 mmol) 3,4-dithio-toluene and 0.2 ml of triethylamine. The mixture was stirred for forty minutes at room temperature, then filtered and washed with cold dry benzene. The residue was recrystallized from ethanol 96% giving 0.35gr of white crystals (yield 55%) m.p. 190-191°C.

IR(KBr): V_{max}: 3319(N-H), 1721(CO), 1625(CO)Cm^{-1}

^1H NMR: ($CDCl_3$) : 2.3(t, 3H, CH_3), 3.3 (s, 1H, SH), 4.35(d, 2H, CH_2),
4.8(s, 1H, SH), 7.3-7.9(m, 9H, ArH), 9.3 (s, 1H, NH) ppm,

^{13}C NMR: ($CDCl_3$) : 20.95, 49,86, 127.6-141.32, 167.5, 195.9 ppm.

Anal calcd. $C_{16}H_{15}O_2NS_2$, C, 60,56%; H, 4.73% N, 4.42%; S, 20.18%.

Found C, 60,20%; H, 4.65%; N, 4.15%; S, 19.9%;

Preparation of 4-Benzylidene-2-Phenyl-5(4H)oxazolone[11].

Benzaldehyde (1mmol) and 2-phenyl-5(4H)oxazolone (1mmol) were mixed and heated together on the water bath for 5-10 min, then poured on ice water. The crude products were separated by filteration, then washed with cold 70% ethanol and recrystallized from ethanol .Yield and m.p. are 63% and 158°C respectively.

Preparation of (2-mercapto-4-methyl-phenyl)-2-benzamido-3-phenyl-thiopropenoate.

To a solution of (0.498 gr, 2 mmol) 4-benzylidene-2-phenyl-5(4H)oxazolone in 30 ml of dry benzene was added (0.312ml, 2 mmol) of 3,4-dithio- toluene and 0.2 ml triethylamine then stirred for 1 hr at room temperature. After filteration the residue recrystallized from benzene giving 157 gr of white crystals (yield 74%) m.p. 208-209 °C.

IR(KBr); V_{max} : 3290 (NH), 1692(CO), 1649(CO)Cm^{-1}

^1H NMR: ($CDCl_3$) : 2.4(t, 3H, CH_3), 4.8(s, 1H, SH),5.4(s, 1H, SH), 6.9-7.7 (m, 14H, CH, ArH), 9.1(s, 1H, NH)ppm,

^{13}C NMR: ($CDCl_3$): 21.1, 54.3, 58.8, 126.8-140.8, 142.3, 166.3, 199.3, ppm.

Anal calcd : $C_{23}H_{19}O_2S_2N$, C, 68.15%; H, 4.69%; N, 3.46; S, 15.80%

Found : C, 67.65%; H, 4.2,5%; N, 3.22%, S, 15.4%

Preparation of 4-cyclohexylidene-2-phenyl-5-(4H)-oxazolone [12].

A mixture of anhydrous sodium acetate (9.0 gr. , 0.1 mol), and hippuric acid (18.0 g., 0.1 mol) and cyclohexanone (30 ml, 0.3mol), and acetic anhydrid (35 ml) was heated with shaking untill the solution had gone from a pinkish semi-sloid to a deep orange liquid (10-15 minutes). The mixture was kept cooled to room temperature and the solid product was separated by filtration. The crude product was recrystallized by ethanol, giving 11.3 g. (49%) of fine, white needle crystals, m.p. 137-138 °C.

Preparation of (2-mercapto-4-methyl-phenyl) 2-benzamido-2-cyclohexylidene--thioethanoate [12]

To a solution of(0.458 gr, 2mmol) 4-cyclohexylidene 2-phenyl-5(4H)oxazolone in 30 ml of dry benzene was added (0.312 ml, 2 mmol) of 3,4-dithio-toluene and 0.2 ml triethylamine, then was stirred for forty minutes at room temperature, after recrystallization from ethanol, giving 0.54 gr of white crystals (yield %68) m.p. 180-181°C.

IR(KBr): V_{max}: 3395 (NH), 1662(CO)Cm^{-1}

^1H NMR: ($CDCl_3$) : 1.06-2.1(m, 10H, CH_2), 2.4(s, 3H, CH_3), 5.1(s, 1H, SH), 6.9-7.74(m, 8H, ArH), 7.90(s. 1H, NH)ppm,

^{13}C NMR: ($CDCl_3$): 21.15, 21.43, 25.38, 30.33, 32.45, 76.33, 77.43, 78.33, 127.63, 127.84, 120.79, 129.25,131.40, 132.15, 133.65, 137.70, 140.1, 166.70, 199.1 ppm.

Anal Calcd: $C_{22}H_{23}O_2S_2N$. C, 66.67%; H, 5.81%; N, 3.53%; S, 16.16%.

Found. C, 66.32%; H, 5.22%, N, 3.2%, S. 15.91%;

Preparation of 2-Benzamido-2-cyclohexyl-7-methyl-1,4-Benzodithian-3-one.

2-pheyl-4-cyclohexylidene-5(4H)-oxazolone (0.458 gr,2 mmol) and (0.312 ml, 2 mmol) of 3,4-dithio- toluene and 0.2 ml triethylamine was mixed well and heated at 120-130°C for the 30 minuts and the mixture was dissolved in the $CHCl_3$. Then the products were separated by column chromatography. Yield and M. P. are 38% and 111-112°C respectively.

lR (KBr): V_{max} : 3404.2 (NH), 1692.4 (CO) , 1660(CO) $Cm^{-1.}$

^{1}HNMR: ($CDCl_3$) : 1.26-2.07 (m, 11H, CH_2), 2.36(s, 3H, CH_3), 6.9-7.5 (m, 8H, ArH) , 7.89 (s, 1H, NH) ppm.

^{13}CNMR: ($CDCl_3$) : 20.73 –21.17, 21.54, 22.40, 25.11, 125.95, 127.24, 127.66, 128.69, 129.14, 131.35, 132.03, 133.55, 137.55, 139.99, 166.42, 199.45 ppm.

Anal Calcd: $C_{22}H_{23}O_2S_2N$. C, 66.67%; H, 5.81%; N, 3.53%; S, 16.16%.

Found: C, 66.32%; H, 5.22%, N, 3.2%, S, 15.91%;

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