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Reaction of 4-Arylidene-2-imidazolin-5-one Derivatives with 3,4-Dithio Toluene in the Presence of Triethylamine

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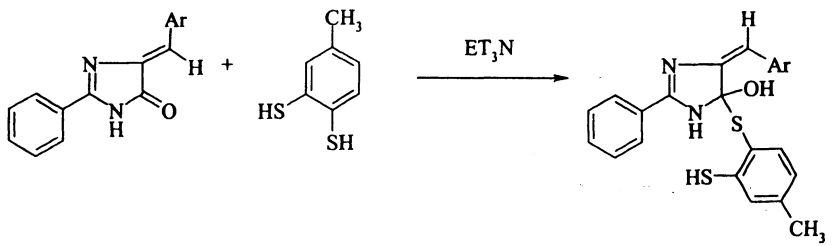
The addition of 3,4-dithio toluene with 2-imidazolin-5-one leads to the 1,4-addition adduct products instead of attack to the carbonyl group as a nucleophile and ring cleavage of imidazolones occurs.

Key Words: 2-Imidazolin-5-one, 3, 4-Dithio toluene.

INTRODUCTION

Unsaturated 2-imidzolin-5-ones, which are the nitrogen analogs of azalactones, form an important class of heterocyclic compounds because they can be converted into α-amino-acids[1, 2] and used in drugs[3], pigments and electrodes[4], etc. In this study, nucleophilic addition of 3,4-dithio toluene in the presence of triethylamine have been investigated. The major product was obtained from 1,4-addition through exocyclic double bond by both available thio groups in meta and para position. Three ways of nucleophilic addition reaction are possible: (1) 1,2-addition, (2) 1,2-addition with ring cleavage and (3) 1,4-addition.

If addition occurs at the carbonyl group of imidazolone then it is converted to hydroxyl group and then loss of one molecule of water takes place[5].



But on the other hand, as we know that imidazolone is in the tautomeric form, therefore we expected that thio group's reaction with carbonyl group should be rare.

To complete the reaction along with ring cleavage seemed very difficult because the stability of the ring will be decayed and it is impossible. Therefore, the thio anion will attack the C=C exocyclic double bond as 1,4-addition and lead to the

product in which these compounds contain aromaticity properties; moreover, imidazolone itself reacts with bromine-water while the product will not react.

EXPERIMENTAL

All chemicals were of reagent grade and used as purchased from the commercial sources. The FTIR spectra were recorded on a Shimadzu DR-8001 Spectrophotometer in the range of 4000–400 cm^{-1}.

Preparation of 4-arylidene-2-imidazol-5-one[4]

In every case 0.01 mol of aromatic aldehyde was condensed with a mixture of 2.5 g of benzamidine hydrochloride dihydrate[5] and 2.5 mL of ethyl chloroacetate in the presence of 3.38 g sodium bicarbonate and 20 mL of *n*-propanol.

The starting material was taken in a 100 mL round-bottomed flask and heated under reflux using an electric mantle; the flask was shaken until boiling began and then shaken occasionally. After a total refluxing the unsaturated 2-imidazolin-5-one began to precipitate. The flask was allowed to cool down at room temperature and the crude product was filtered in a glass funnel. It was first washed with 10 mL of methanol, then thrice with 10 mL portions of water and finally with 5 mL of methanol and dried. The product was recrystallized from ethanol or ethyl acetate[7].

Preparation of 5-{(4-hydroxy-2-methoxyphenyl)[(4-methyl-2-sulfanyl]-methyl}-2-phenyl-3,5-dihydro-4H-imidazol-4-one (A)

1.52 g (0.01 mol) of 4[(Z,E)-1-(2-hyroxy-4-methoxyphenyl)methylidene-2-phenyl-1H-imidazol-5-one was added to fresh dry DMF (5–10 mL) and heated on an oil bath while stirring till imidazolone disappeared. 1.5 mL (0.012 mol) of 3,4-dithio toluene was added by syringe; the solution became orange by adding triethylamine dropwise; the colour changed to deep red solution; then it was refluxd for 1 h.

After 1 h heating, the temperature must be reduced slowly. Residue must be cooled and triturated with ethanol and the solid obtained is filtered, washed with methanol and then ethyl acetate. Finally, the product recrystallized by 2-propanol (m.p. 145–147°C). IR (KBr, cm^{-1}) ν_{max}: 3438 ν(N—H), 2663 ν(CH_3), 1701 ν(C=O), 1641 ν(C=N), 1601 ν(C=C). ^1H NMR: ($CDCl_3$): 1.71 (s, 3H, CH_3), 4.19 (s, 1H, OH), 4.04 (s, 3H, OCH_3), 4.20 (s, 1H, SH), 6.8–8.3 (m, 11H, Ar—H), 11.28 (s, 1H, N—H) ppm. ^{13}C NMR ($CDCl_3$): 10.15, 21.80, 55.86, 65.91, 66.05, 112.9–149.5, and 168.5 ppm. Anal (%) Calcd. $C_{24}H_{22}N_2O_3S_2$: C, 64.00; H, 4.90; N, 6.22. Found C, 64.12; H, 4.93; N, 6.37.

Preparation of 5-{2-furyl[(4-methyl-2-sulfanylphenyl)sulfanyl]methyl}-2-phenyl-3,5-dihydro-4H-imidazol-4-one (B)

2.3 g (0.01 mol) of 5-[(Z,E)-1-(2-furyl) methylidene]-2-phenyl-3,5-dihydro-4H-imidazol-4-one was weighed and added into fresh dry DMF (5–10 mL) and heated on an oil bath while stirring till imidazolone disappeared. 1.5 mL (0.012

mol) of 3,4-dithio toluene was added by syringe; the solution became orange by adding triethylamine dropwise; the colour changed to deep red; then it was refluxed for 1 h. After 1 h heating, the temperature was reduced slowly. The residue was cooled and triturated with ethanol and the solid was filtered. The product was washed with methanol and then with ethyl acetate. Finally, the product was recrystallized from ethanol (m.p. = 178–1797°C). IR (KBr, cm^{-1}) ν_{max}: 3456 ν(N—H), 3136 ν(C—H), 2929 ν(C—H), 1706 ν(C=O), 1648 ν(C=N), 1612 ν(C=C). ^{1}H NMR ($CDCl_3$): 2.23 (1, 3H, CH_3), 2.89 (s, 1H, CH), 2.97 (s, 1H, CH), 2.97 (s, 1H, CH), 3.13 (s, 1H, CH), 4.14 (s, 1H, S—H), 6.65–8.07 (s, 11H, Ar—H), 9.8 (s, 1H, N—H) ppm. ^{13}C NMR ($CDCl_3$): 8.73, 20.9, 22.7, 29.72, 31.41, 36.53, 45.87, 113, 119-132, 146 ppm. Anal. (%) Calcd. $C_{21}H_{18}N_2O_2S_2$: C, 63.95; H, 4.56; N, 7.10. Found C, 64.10; H, 4.48; N, 6.93.

Preparation of 5-{[4-chlorophenyl){4-methyl-2-sulfanylphenyl)sulfanyl]-methyl}-2-phenyl-3,5-dihydro-4H-imidazol-4-one (C)

2.82 g (0.01 mol) of 4-[(Z,E)-1-(4-chlrophenyl)methylidene]-2-phenyl-1H-imidazol-5-one was weighed and added into fresh dry DMF (5–10 mL) and heated on an oil bath while stirring till imidazolone disappeared. 1.5 mL (0.012 mol) of 3,4-dithio toluene was added by syringe; the solution became orange by adding triethylamine dropwise; the colour changed to purple and then it was refluxed for 1 h. After 1 h heating the temperature was reduced slowly. The residue was cooled and triturated with ethanol and the solid was filtered. The product was washed with methanol and then ethyl acetate and the product was recrystallized from 2-propanol (m.p. = 210–212°C).

IR (KBr, cm^{-1}) ν_{max}: 3434 ν(N—H), 2931 ν(C—H), 1703 ν(C=O), 1647 ν(C=N), 1602 ν(C=C). ^{1}H NMR ($CDCl_3$): 2.28 (s, 3H, CH_3), 3.62 (s, 1H, CH), 3.79 (s.1H, CH), 4.07 (s, 1H, S—H), 6.88–7.41 (m, 12H, Ar—H), 9.8 (s, 1H, N—H) ppm. ^{13}C NMR ($CDCl_3$): 13.92, 19.30, 21.28, 31.65, 69.68, 71.72, 109.61–128.27, 139, 142 ppm. Anal. (%) Calcd. $C_{23}H_{19}N_2OS_2Cl$: C, 62.93; H, 4.36; N, 6.38. Found C, 62.47; H, 4.52; N, 6.29.

Preparation of 5-{(2,4-dichlorophenyl)[(4-methyl-2-sulfanylphenyl)-sulfanyl]methyl}-2-phenyl-3,5-dihydro-4H-imidazol-4-one (D)

3.17 g (0.01 mol) of 4-{(Z,E)-1-(2,4-dichlorophenyl)methylidene]-2-phenyl-imidazol-5-one was weighed and added into fresh dry DMF (5–10 mL) and heated on an oil bath while stirring till imidazolone dissolved. 1.5 mL (0.012 mol) of 3,4-dithio toluene was added by syringe; the solution became orange by adding triethylamine dropwise; the color changed to deep red; then it was refluxed for 1 h. After 1 h heating, the temperature was reduced slowly. The residue was cooled to room temperature and triturated with ethanol and the solid was filtered; the product was washed with a few mL of methanol and then ethyl acetate and recrystallized from iso-propanol (m.p. = 158–160°C). IR (KBr, cm^{-1}) ν_{max}: 3433 ν(C—H), 2928 ν(C—H), 1714 ν(C=O), 1647 ν(C=N), 1610 ν(C=C). ^{1}HNMR

($CDCl_3$): 2.21 (s, 3H, CH_3), 3.12 (s, 1H, S—H), 5.2 (s, 1H, CH), 4.75 (s, 1H, CH), 6.72–7.96 (m, 11H, Ar—H), 10.40 (s, 1H, N—H) ppm. ^{13}C NMR ($CDCl_3$): 20.48, 32.57, 74.01, 128.06–153, 165.86 ppm. Anal. (%) Calcd. $C_{23}H_{18}N_2S_2Cl_2$: C, 58.35; H, 3.83; N, 5.92. Found : 58.70; H, 4.10; N, 5.80.

Preparation of 5-[[4-methyl-2-sufanylphenyl)sulfanyl](phenyl)methyl]-2-phenyl-3,5-dihydro-4H-imidazol-4-one (E)

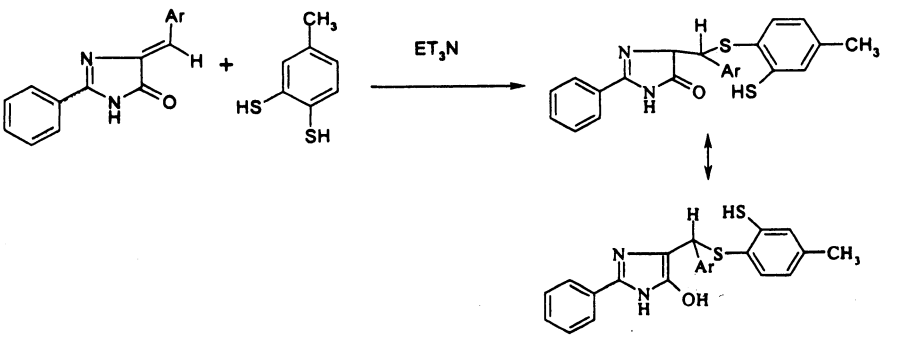
2.48 g (0.01 mol) of -phenyl-4-[(Z, E)-1-phenyl-methylidene]-1H-imidazol-5-one was weighed and added into fresh dry DMF (5–10 mL) and heated on an oil bath while stirring till imidazolone dissolved. 1.5 mL (0.012 mol) of 3,4-dithio toluene was added by syringe; the solution became orange by adding triethylamine drop wise; with addition of triethylamine the colour of the solution changed to deep red; then it was refluxed for 1 h. After 1 h heating, the temperature was reduced slowly. The residue was cooled and triturated with ethanol and the solid filtered. The product was washed with a few mL of methanol and then ethyl acetate. The product recrystallized from *n*-propanol (m.p. = 215–217°C). IR (KBr, cm^{-1}) ν_{max}: 3438 ν(N—H), 2987 ν(C—H), 1720 ν(C=O), 1650 ν(C=N), 1615 ν(C=C). ^1H NMR ($CDCl_3$): 2.2 (s, 3H, CH_3), 4.89(s, 1H, S—H), 4.56 (s, 1H, CH), 4.86 (s, 1H, CH), 6.58–7.88 (m, 13H, Ar—H), 8.88 (s, 1H, N—H) ppm. ^{13}C NMR: ($CDCl3$): 20.54, 64.70, 74.99, 127-137, 150, 170 ppm. Anal (%) Calcd. $C_{23}H_{20}N_2OS_2$: C, 68.28; H, 4.98; N, 6.93. Found: C, 68.50; H, 4.60; N, 7.20.

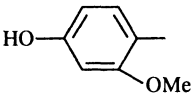
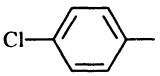
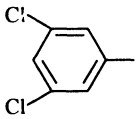
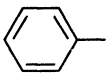
RESULTS AND DISCUSSION

2-imidazolin-5-one, when mixed with 3,4-dithio toluene at high temperature in the presence of triethylamine, gives a new product. It seems that 3,4-dithio toluene reacts as nucleophilic reagent to C=C exocyclic double bond.

It is notable that both thio groups, meta and para position, are able to attack; therefore, the isomeric products is expected; but the thio group in para postion is more reactive than meta and then one of these isomers is the major product.

If 4-arylidene-2-imidazolin-5-one is mixed with 3,4-dithio toluene in the presence of triethylamine at constant oil bath temperature, the 1,4-addition will be occurring as the following reactions:



Ar	m.p. (°C)	Compd.
	145–147	A
	178–179	B
	210–212	C
	158–160	D
	215–217	E

Similar reactions were carried out with Grignard reagents in which 1,4-addition reaction takes place[6].

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