SYNTHESIS OF 5-SUBSTITUTED 4-METHYLTHIO-1,3-THIAZOLINE -2-THIONES

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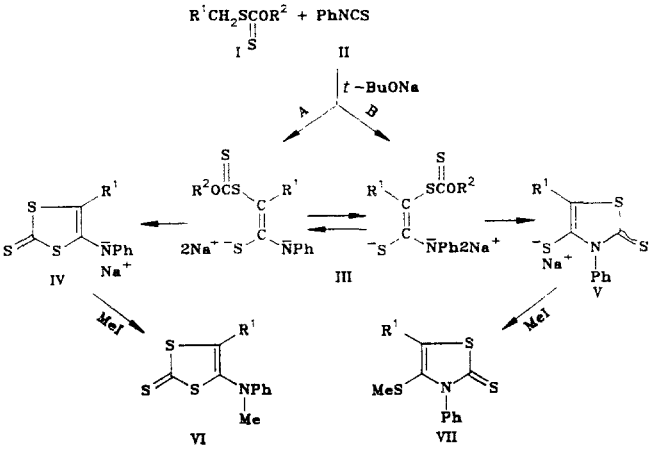
In order to study the cyclization pathway we investigated the reaction of alkyl esters of S-alkoxycarbonylmethyl- and S-cyanomethylxanthogenic acids with phenyl isothiocyanate in the presence of strong bases. In contrast to the known reaction with carbon disulfide [1], two pathways – A and B – are possible in this case.



R^1=COOMe, COOEt, CN; R^2=Me, Et

1,3-Dithiole-2-thiones, the formation of which is possible via pathway A, are starting compounds for the synthesis of tetrathiafulvalenes; 4-alkylthio-1,3-thiazoline-2-thiones (pathway B) have not been described heretofore, and their analogs are of interest as potential biologically active substances [2].

We have established that the reaction proceeds primarily via pathway B with the formation, after methylation, of 4-methylthio-1,3-thiazoline-2-thiones. Thus methyl ester VII was obtained in the condensation of methyl methoxycarbonylmethylxanthogenate (I, R^1 = COOMe, R^2 = Me) with phenyl isothiocyanate (II) in DMF in the presence of sodium tert-butoxide with subsequent alkylation with methyl iodide.

Methyl 4-Methylthio-2-thioxo-3-phenyl-1,3-thiazoline-5-carboxylic Acid (VII, R^1 = COOMe). This compound was obtained in 45% yield in the form of yellowish crystals with mp 171°C and Rf 0.32 (Silufol, benzene). IR spectrum (mineral oil): 1732, 1595, 1533, 1490, 1310, 1235, 1080 cm^{-1}. UV spectrum (ethanol), λ_{max} (log ε): 309 (3.98), 350 (4.12). PMR spectrum ($CDCl_3$): 2.25 (3H, s, SMe), 3.81 (3H, s, OMe), 7.25 and 7.48 ppm (5H, m, NPh). The structure was confirmed by the results of x-ray diffraction analysis, regarding which a separate communication will follow.

The following VII were similarly obtained.

Ethyl 4-Methylthio-2-thioxo-3-phenyl-1,3-thiazoline-5-carboxylate (VVI, R^1 = COOEt). This compound was obtained in 40% yield in the form of yellow crystals with mp 132°C. PMR spectrum ($CDCl_3$): 1.33 (3H, t, Me), 2.25 (3H, s, SMe), 4.32 (2H, q, CH_2), 7.25 and 7.48 ppm (5H, m, NPh).

4-Methylthio-3-phenyl-5-cyano-1,3-thiazoline-2-thione (VII, R^1 = CH). This compound was obtained in 44% yield in the form of a light-brown powder with mp 211°C. IR spectrum

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(mineral oil): 2210, 1590, 1523, 1483, 1348, 1306, 1237, 1053 cm^{-1} UV spectrum (ethanol), λ_{max} (log ε): 268 (3.92), 312 (3.91), 348 (4.15). PMR spectrum ($CDCl_3$): 252 (3H, s, SMe), 7.30 and 7.54 ppm (5H, m, NPh).

The results of elementary analysis of the compounds were in agreement with the calculated values.

LITERATURE CITED

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2. GDR Patent 239593, W. Dölling, M. Augustin, and P. Kindt, Ref. Zh, Khim., 7N204P (1986).

NEW HETEROCYCLIC SYSTEM — 5,6,7,8-TETRAHYDRO-4H-THIAZOLO[5,4-c]-AZEPIN-8-ONE

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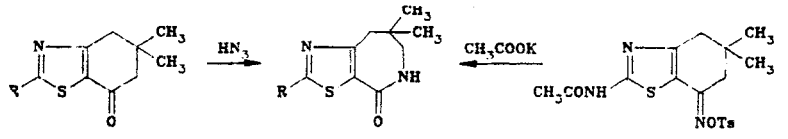
It was shown that 4,5,6,7-tetrahydrobenzo-7-thiazolone derivatives I, under the conditions of the Schmidt reaction, undergo rearrangement to the corresponding thiazolo[5,4-c]-azepin-8-one derivatives II in good yields. Compound IIb was also obtained from p-toluenesulfonate III by the Beckmann rearrangement, but the yield was low. Isomeric compounds — thiazolo[5,4-b]azepin-8-one derivatives — were not detected in the reaction mixtures in either case



I II a R=NH_2; b R=NHCOCH$_3$

2-Amino-5,5-dimethyl-5,6,7,8-tetrahydro-4H-thiazolo[5,4-c]-azepin-8-one (IIa). A 3.6-mmole sample of sodium azide was added in portions with stirring in the course of 2 h to a solution of 3.3 mmole of Ia in a mixture of 30 ml of chloroform and 2.1 ml of concentrated H_2SO_4. The mixture was stirred at the same temperature for 3 days. The chloroform was decanted, the sulfuric acid solution was poured over ice, and the aqueous mixture was neutralized with a concentrated solution of sodium carbonate at 0-10°C. The resulting precipitate was removed by filtration to give IIa, with mp 259-260°C, in 77% yield. IR spectrum (KBr): 3430, 3300, 2935, 1600, 1515, 1330, 1250, 990 cm^{-1}. PMR spectrum (d_6-DMSO): 1.05 (6H, s, Me_2C), 2.68 (2H, s, 4-H), 3.00 (2H, d, J = 5.7 Hz, 6-H), 7.50 (2H, s, NH_2), 7.70 ppm (1H, t, J = 5.7 Hz, NH). M^+ 211.

2-Acetamido-5,5-dimethyl-5,6,7,8-tetrahydro-4H-thiazolo[5,4-c]-azepin-8-one (IIb). This compound with mp 288-289°C, was similarly obtained in 74% yield either by the Beckmann rearrangement of III, obtained by the action of p-toluenesulfonyl chloride on the corresponding oxime and used in the reaction without purification. IR spectrum (KBr): 3490, 3230, 3130, 3000, 2915, 1600, 1510, 1400, 1330, 1260, 1050, 970, 950 cm^{-1}. PMR spectrum (d_6-DMSO): 1.06 (6H, s, Me_2C), 2.22 (3H, s, MeC=O), 2.85 (2H, s, 4-H), 3.60 (2H, d, J = 5.3 Hz, 6-H), 7.03 (1H, t, J = 5.3 Hz, HN_7), 12.33 pp (1H, s, HN—COMe). M^+ 253.

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