SYNTHESIS OF 2-ARYL-4-PHENYL(AND 2-THIENYL)-1,3-THIAZINE-6-THIONES

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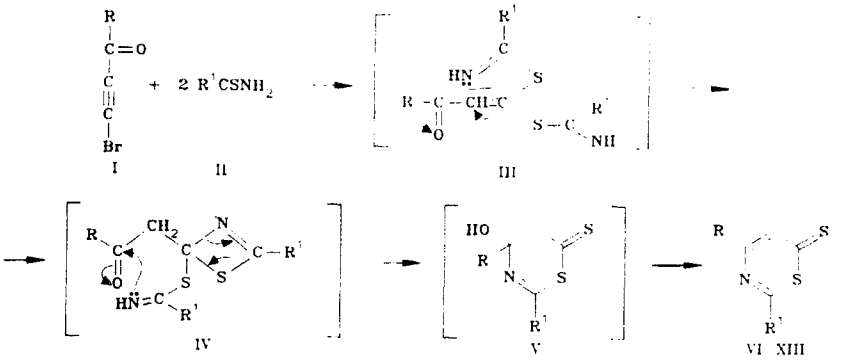
1,3-Thiazine salts are obtained by reacting thioamides with vinyl ketones [1], β-chlorovinyl ketones [2, 3], and α-acetylenic ketones [4] in acetic acid in the presence of perchloric acid.

We have found that the reaction between 1-bromo-2-acylacetylenes (I) and aromatic thioamides (II) at a molar ratio of reagents of 1:2 in glacial acetic acid in the presence of $BF_3 \cdot Et_2O$ at 35-40°C affords high yields of the 1,3-thiazine-6-thiones (VI-XIII).

The reaction probably involves the intermediate formation of the α-ketoketene mercaptals (III), which in the presence of $BF_3 \cdot Et_2O$ undergo intramolecular cyclization to give the 1,3-thiazine-6-thiones (VI-XIII) with the elimination of a molecule of aryl nitrile and of water.



VI R = R¹ = Ph; VII R = 2-thienyl R¹ = Ph; VIII R = Ph, R¹ = *p*-MeC$_6$H$_4$; IX R = 2-thienyl R¹ = *p*-MeC$_6$H$_4$; X R = Ph, R¹ = *p*-ClC$_6$H$_4$; XI R = 2-thienyl R¹ = *p*-ClC$_6$H$_4$; XII R = Ph, R¹ = *p*-NO$_2$C$_6$H$_4$; XIII R = 2-thienyl R¹ = *p*-NO$_2$C$_6$H$_4$

Compound (VIII). mp 161-163°C (from ethanol–chloroform, 10:1). Yield 61%. IR spectrum (KBr): 1535 (C=C), 1465 (C=N), 690 cm^{-1} (C–S). PMR spectrum ($CDCl_3$): 2.40 (s, 3H, CH_3); 7.30-8.08 ppm (10H, m, C_6H_5, C_6H_4, CH=). ^{13}C NMR spectrum ($CDCl_3$): 21.73 (CH_3); 204.14 (C=S); 174.03 ($C_{(2)}$); 152.00 ($C_{(4)}$); 121.06 ($C_{(6)}$); 127.12-144.46 ppm (m, C_6H_5, C_6H_4, 8 signals). Mass spectrum, m/z: 295 $[M]^+$, 251 $[M - (C=S)]^+$, 101 $[Ph–C\equiv C]^+$.

Compound (VI). mp 131-132°C (from ethanol); yield 54%. **Compound (VII).** mp 164-166°C (from ethanol); yield 47%. **Compound (IX).** mp 183-185°C (from ethanol–chloroform); yield 51%. **Compound X.** mp 140-141°C (from ethanol); yield 59%. **Compound (XI).** mp 182-184°C (from ethanol); yield 59%. **Compound (XII).** mp 191-192°C (from ethanol–chloroform); yield 78%. **Compound (XIII).** mp 205-207°C (from ethanol–chloroform); yield 75%.

The elemental analyses of the compounds obtained agreed with the calculated values.

LITERATURE CITED

1. H. Hartman, *Tetrahedron Lett.*, No. 38, 3977 (1972).
2. W. Schroth, R. Spitzner, B. Koch, S. Freitag, and D. Mielke, *Tetrahedron*, **38**, 937 (1982).
3. R. Spitzner, D. Mielke, D. Scholz, and W. Schroth, *Tetrahedron*, **38**, 927 (1982).
4. T. E. Glotova, A. S. Nakhmanovich, and N. S. Mabarakshina, *Khim. Geterotsikl. Soedin.*, No. 5, 705 (1988).

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