1-AMINO-3-ALKYLBENZIMIDAZOLINE-2-THIONES (SELENONES)

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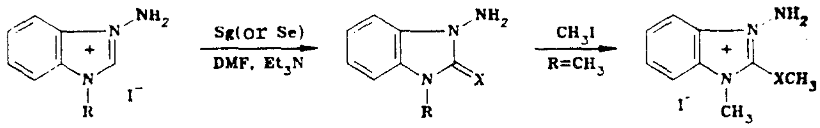
UDC 547.785.5.781.5:546.22.23

We have shown that the reaction of 1-amino-3-alkylbenzimidazolium salts (I) with elemental sulfur in refluxing DMF in the presence of triethylamine gives the previously unknown 1-amino-3-alkylbenzimidazoline-2-thiones (II) in good yields. Similar reaction with selenium gives the selenones III. Compounds II and III are readily alkylated by alkyl halides at the sulfur or selenium to give the salts IV or V. The latter, and the precursors II and III, are promising synthons for a number of condensed systems because of the high susceptibility of the SCH_3 or $SeCH_3$ to nucleophilic substitution.



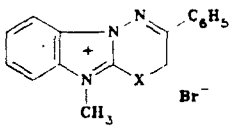
I a, b

II a, b X=S

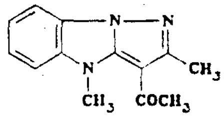
III a, b X=Se

IV X=S; V X=Se

I–III a R=CH_3, b R=C_2H_5



VI X=S; VII X=Se



VIII

Thus, reaction of the thione IIa with phenacyl bromide gives 1,3,4-thiadiazino[3,2-*a*]benzimidazolium bromide (VI) in 88% yield. The analogous selenone IIIa is converted to the selenodiazine VII. The pyrazolo[1,5-*a*]benzimidazole VIII, obtained before by another method [1], is formed in 62% yield from salt IV and acetyl acetone in the presence of sodium tert-butylate.

1-Amino-3-methylbenzimidazoline-2-thione (IIa, $C_8H_9N_3S$). A solution of 1-amino-3-methylbenzimidazolium iodide (Ia, 0.1 mole) [2], elemental sulfur (0.1 mole), and triethylamine (0.1 mole) in DMF (10 ml) is refluxed for 1 h and poured into water (30 ml). The precipitate is filtered off and washed with water, alcohol, and ether to give product (81%) with mp 152-153°C (from benzene). IR spectrum (Vaseline mull): 1590, 1645, 3172, 3274 cm^{-1} (NH_2).

1-Amino-3-ethylbenzimidazoline-2-thione (IIb, $C_9H_{11}N_3S$). Mp 92-93°C (from octane). IR spectrum (Vaseline mull): 1542, 1632, 3170, 3270 cm^{-1} (NH_2). Yield 69%.

1-Amino-3-methylbenzimidazoline-2-selenone (IIIa, $C_8H_9N_3Se$). Mp 170-171°C (from benzene). IR spectrum (Vaseline mull): 1645, 3168, 3265 cm^{-1} (NH_2). Yield 80%.

1-Amino-3-ethylbenzimidazoline-2-selenone (IIIb, $C_9H_{11}N_3Se$). Mp 116-117°C (from alcohol). IR spectrum (Vaseline mull): 1640, 3174, 3290 cm^{-1} (NH_2). Yield 71%.

1-Amino-3-methyl-2-methylthiobenzimidazolium Iodide (IV, $C_9H_{12}IN_3S$). Mp 140-142°C (decomp. from alcohol). IR spectrum (Vaseline mull): 1627, 3140, 3237 cm^{-1} (NH_2). PMR spectrum (DMSO-D_6): 2.83 (3H, s, SCH_3); 4.03 (3H, s, NCH_3); 6.88 (2H, m, NH_2, lost on deuteration); 7.66 (2H, m, arom.); 7.93 ppm (2H, arom.). Yield 96%.

1-Amino-3-methyl-2-methylselenobenzimidazolium Iodide (V, $C_9H_{12}IN_3S$). Mp 120-121°C (decomp.). IR spectrum (Vaseline mull): 1630, 3100, 3205 cm^{-1} (NH_2). Yield 95%.

Scientific-Research Institute for Physical and Organic Chemistry, Rostov State University, Rostov-on-Don 344006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1689-1690, December, 1990. Original article submitted February 2, 1990.

0009-3122/90/2612-1406$12.50

10-Methyl-3-phenyl-2H-1,3,4-thiadiazino[3,2-*a*]benzimidazolium Bromide (VI, $C_{16}H_{14}BrN_3S$). Mp 233-234°C (from water.). PMR spectrum (DMSO-D_6): 4.05 (3H, s, NCH_3); 4.9 (2H, s, CH_2); 7.66 (5H, m, arom.); 8.1 ppm (4H, m, arom.). Yield 88%.

10-Methyl-3-phenyl-2H-1,3,4-selenodiazino[3,2-*a*]benzimidazolium Bromide (VII, $C_{16}H_{14}BrN_3S$). Mp 252-253°C (decomp., from water.). Yield 98%.

LITERATURE CITED

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1,3-DIPOLAR CYCLOFRAGMENTATION OF A SPIROANNELATED TETRAZOLE

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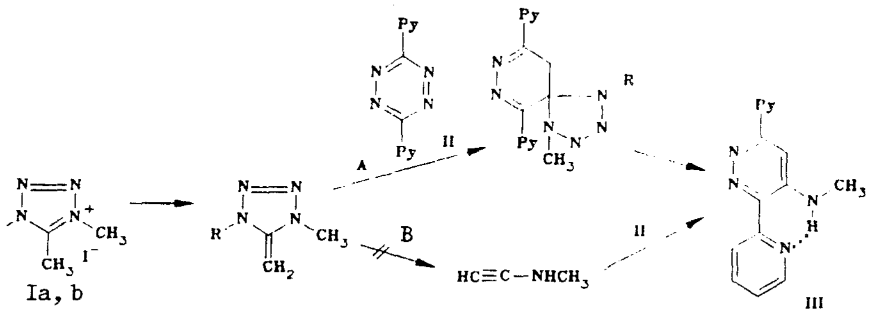
UDC 547.883.796.1

The anhydro-bases of six-membered heterocycles (acridines, xanthenes, thioxanthenes [1, 2], and quinoxalines [3]) have been shown to be capable of participating in cycloaddition reactions. The π-excessive nature of five-membered heterocycles reduces the acidity of their salts, thereby preventing the formation of anhydro-bases on treatment with tertiary amines (hydroxylic bases decompose s-tetrazines, but azolium cations usually convert them into the pseudobases). In the case of the five-membered heterocycle with the best acceptor properties, however (tetrazole), we have been able to carry out the reaction under the usual conditions. On boiling an alcoholic suspension of the tetrazolium iodide (I) and 3,5-di-(2-pyridyl)-s-tetrazine (II) in the presence of triethylamine, there was obtained 90% of 4-methylamino-3,6-di-(2-pyridyl)pyridazine (III) as bright yellow needles, mp 207-209°C (from heptane). PMR spectrum (in DMSO-D_6): 3.07 (3H, d, J = 5 Hz, N–CH_3); 9.85 (1H, m, NH); 7.5-8.9 ppm (protons of the α-pyridyl and pyridazine moieties). IR spectrum: 3235 cm^{-1} (ν_{NH}, intramolecular hydrogen bond). UV spectrum (in ethanol), λ_{max}, nm (log ε): 260 (4.03), 282 (4.32), 262 (3.93). M^+ 263.

GLC analysis of the reaction products of (Ia) with (II) showed the presence of substantial amounts of phenyl azide. However, when the salt (Ia) was treated with triethylamine in the absence of the tetrazine, phenyl azide was not formed, nor was methylaminoacetylene, which would be expected to be a synthon in cycloaddition to the tetrazine to give the pyridazine (III). The reaction may thus be described as the cycloaddition of the anhydro-base of the tetrazolium salt followed by 1,3-dipolar cyclofragmentation of the spiro-coupled tetrazole (route A).



Py = 2- pyridyl ., Ia R = C_6H_5; R = CH_3

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