DESULFURATION OF DERIVATIVES OF PYRIMIDO-, PYRAZINO-, AND PYRIDO[1,4]THIAZINES

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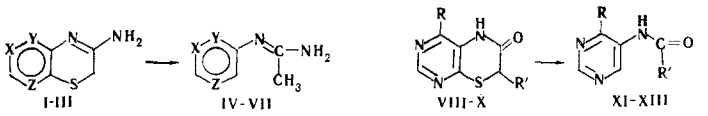
UDC 547.869'853.543.422.4

Tetrahydrocarbazole has been obtained by the desulfuration of tetrahydrophenothiazine derivatives by means of Raney nickel [1]. In an investigation of the properties of condensed bicyclic 1,4-thiazine systems [2] we found that N-(5-pyrimidyl)-, N-(3-pyrazinyl)-, and N-(3-pyridyl)acetamidines (IV-VII) are formed by the desulfuration of 6-aminopyrimido[4,5-b]-, pyrazine[2,3-b]-, and pyrido[2,3-b][1,4]thiazines (I-III). 4-Methoxy-5-acylaminopyrimidines (XI and XII) and 4-hydroxy-5-acylaminopyrimidines (XIII) are similarly obtained from 4-methoxypyrimido[4,5-b][1,4]thiazin-6-ones and 4-methoxy-7-carbethoxymethyl- and 4-hydroxy-7-carbethoxymethylpyrimido[4,5-b][1,4]thiazin-6-ones (VIII-X). The structures of the compounds obtained were confirmed by the IR and PMR spectra.



I-III IV-VII VIII-X XI-XIII

I Z = X = N, Y = CH; II Z = Y = N, X = CH; III X = Y = CH, Z = N; VIII-X R = OCH_3, OH; R' = H, $CH_2CO_2C_2H_5$; XI-XIII R = OCH_3, OH; R' = CH_3, $CH_2CO_2C_2H_5$

EXPERIMENTAL

N-(4-Methoxy-5-pyrimidyl)acetamidine (IV). This was obtained in 70% yield and had mp 140-142° (benzene). PMR spectrum (D_2O): 2.08 ppm [N=C(CH_3)NH_2], 6.79 ppm (6-CH=), 7.188 ppm (2-CH=). Found %: C 50.48; H 5.91; N 33.62. $C_7H_{10}N_4O$. Calculated %: C 50.59; H 6.07; N 33.71.

N-(2-Amino-4-methyl-5-pyrimidyl)acetamidine (V). This was obtained in 82% yield and had mp 165-167° [benzene–ethanol (20:1)]. PMR spectrum (D_2O): 2.12 ppm [N=C(CH_3)–H_2], 7.86 ppm (6-CH=). Found %: C 50.97; H 6.57; N 42.05. $C_7H_{11}N_5$. Calculated %: C 50.89; H 6.70; N 42.40.

N-(2,3-Dimethyl-5-pyrazinyl)acetamidine (VI). This was obtained in 78% yield and had mp 128-130° (hexane). PMR spectrum ($CHCl_3$): 2.11 ppm [N=C(CH_3)NH_2], 2.37 ppm (2-CH_3), 8.13 ppm (6-CH=). Found %: C 58.24; H 7.12; N 34.24. $C_8H_{12}N_4$. Calculated %: C 58.51; H 7.36; N 34.13.

N-(2-Methoxy-3-pyridyl)acetamidine (VII). This compound had mp 134-136° (benzene). Found %: C 58.40; H 6.96; N 25.30. $C_8H_{11}N_3O$. Calculated %: C 58.16; H 6.71; N 25.40.

4-Methoxy-5-acetamidopyrimidine (XI). This was obtained in 83% yield and had mp 162-164° (benzene). IR spectrum (cm^{-1}): 1700 (CO–NH), 3220 (NH). Found %: C 50.58; H 5.65; N 24.98. $C_7H_9N_3O_2$. Calculated %: C 50.29; H 5.43; N 25.14.

4-Methoxy-5-(β-carbethoxypropionylamino)pyrimidine (XII). This was obtained in 48% yield and had mp 85-87° (ether). IR spectrum (cm^{-1}): 1695 (CO–NH), 1733 ($COOC_2H_5$), 3330 (NH). Found %: C 52.55; H 6.12; N 16.67. $C_{11}H_{15}N_3O_4$. Calculated %: C 52.17; H 5.97; N 16.69.

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 423-424, March, 1971. Original article submitted April 27, 1970.

4-Hydroxy-5-(carbethoxyacetamido)pyrimidine (XIII). This was obtained in 72% yield and had mp 186-187° (ethanol). Found %: C 48.00; H 5.18; N 18.65. $C_9H_{11}N_3O_4$. Calculated %: C 48.00; H 4.92; N 18.66.

LITERATURE CITED

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2. T. S. Safonova, in: Modern State of the Chemotherapy of Malignant Tumors [in Russian], Riga (1968), p. 37.