s, H_2O), 6.85 (4H, s, C_6H_4), 7.38-8.18 ppm (6H, m, Ar + OCHO). Elemental analytical data was in agreement with that calculated.

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REACTION OF 4-METHOXY(METHYLTHIO)-5-AMINO-6-MERCAPTOPYRIMIDINES WITH ω,ω-DIBROMOACETOPHENONE

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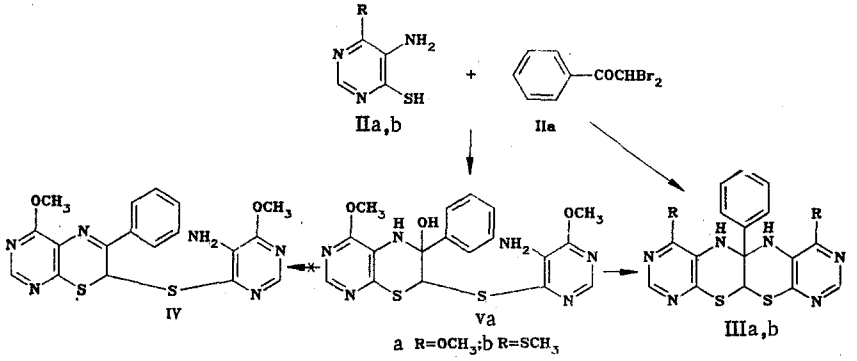
UDC 547.854.83'869.2.07

It is known that reaction of 5-amino-6-mercaptopyrimidines with ω-haloacetophenones gives 6-aryl-6-hydroxy-5H-6,7-dihydropyrimido[4,5-b][1,4]thiazines which are readily dehydrated to 6-aryl-7H-pyrimido[4,5-b][1,4]thiazines [1].

We have found that the reaction of 4-methoxy- and 4-methylthio-5-amino-6-mercaptopyrimidines (Ia,b) with ω,ω-dibromoacetophenone (under conditions for the synthesis of 6-aryl-7H-pyrimido[4,5-b][1,4]thiazines) unexpectedly produces 4,7-dimethoxy(dimethylthio)-5a-phenyl-pyrimido[4,5-b][1,4]thiazino[7,8-g]pyrimido[4,5-b][1,4]thiazines (IIIa,b) which represent a new heterocyclic system.

The product expected was 6-aryl-7H-pyrimido[4,5-b][1,4]thiazine (IV) (substituted at the 7-position) but this was not formed in the reaction.

In the case of Ia and IIa it was possible to separate the cyclic carbinol, Va, which is postulated intermediate in this process. It may be converted to IIIa but not to IV.



Compounds IIIa,b and Va were crystalline materials, stable on standing.

IIIa: mp 243-245°C (DMFA–water), yield 66%
IIIb: mp 253-254°C (DMFA–water), yield 64%
Va: mp 165-167°C (methanol), yield 80%

Elemental organic analytical data agreed with that calculated and IR, UV and PMR spectra confirmed the structures proposed for IIIa,b and Va.

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Benzo-analogs of the tetracyclic system IIIa,b have been obtained previously by reaction of o-aminothiophenol with cyclohexanone [2].

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NEW SYNTHESIS OF 1-VINYL- AND 1,3-DIVINYLURACILS

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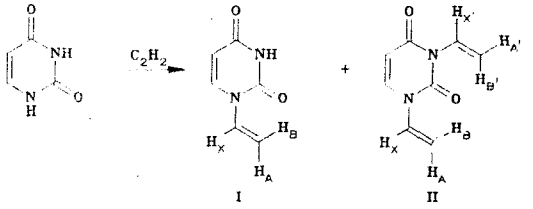
UDC 547.854.4'314.2.07

It has previously been reported that 2-pyridone reacts with acetylene in the presence of cadmium acetate preferentially forming 2-vinyloxypyridine, while vinylation proceeds at the second reaction center, the nitrogen atom, in the presence of potassium hydroxide [1]. The sensitivity of the pyrimidine ring to alkaline agents precludes the use of alkali metal hydroxides as catalysts during the vinylation of uracil. We have found that the reaction of uracil with acetylene, catalyzed by cadmium acetate, leads in one step to the synthesis of N-substituted mono- and divinyluracils. As products of the reaction, two compounds were isolated: 1-vinyluracil (I), mp 180°C and 1,3-divinyluracil (II), mp 60°C. The process temperature conditions were varied between 200-240°C, and the yields of compounds I and II reached 20-43%.

The structure of compounds I and II was confirmed by the hydrogenation of the vinyl groups, by IR and PMR spectra. The individuality of the compounds was confirmed by TLC on aluminum oxide: R_f 0.155 (benzene–ethyl acetate–methanol, 1:1:1) and 0.824 (benzene–ethyl acetate, 1:1) for compounds I and II, respectively. The physical constants of compound I obtained by direct vinylation coincide with those for compound I obtained by a two-step method [2].



The position of the second vinyl group in divinyluracil was determined by the analysis of PMR spectra. The values of the vicinal SSCC in compound II (J_{cis} 9.0-9.2 and J_{trans} 15.4-16.0 Hz) indicate the presence of two vinyl groups joined to nitrogen atoms [3].

IR spectrum (with KBr): for compound I, 3100, 1635, 975 ($CH=CH_2$), 1713, 1690 (C=O), 3160 cm^{-1} (NH); for II, 3100, 1640, 975, 965 ($CH=CH_2$), 1720, 1690 cm^{-1} (–C=O). There is no absorption in the 3380-3160 cm^{-1} region. PMR spectrum ($CDCl_3$): for I, 4.95, 5.08, 7.18 (ABC protons of the vinyl group, d.d. J_{AB} = 2.2, J_{AC} = 8.4., J_{BC} = 16.4 Hz), 5.78 (SH, d) 7.46 (6H, d, J_{56}=8.0 Hz), 10.3 ppm (NH, br. s); for II, 4.95, 5.06, 7.16, and 5.26, 5.87, 6.80 (ABC and A'B'C' protons of the two vinyl groups, d.d. J_{AB} 2.3, $J_{A'B'}$ = 0, J_{AC} = 9.0, $J_{A'C'}$ = 9.2, J_{BC} = 15.6, $J_{B'C'}$ = 16.0 Hz), 5.79 (5-H, d), 7.40 (6-HJ, d, J_{56} = 8.0 Hz).

The elemental analysis and molecular weights (mass spectrometrically) of uracils I and II correspond to the calculated values.

*Deceased.

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