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

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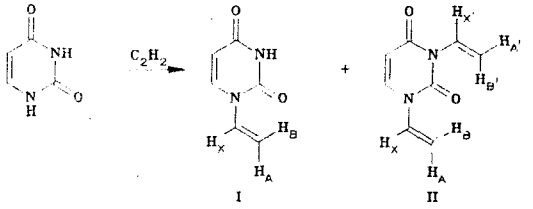
NEW SYNTHESIS OF 1-VINYL- AND 1,3-DIVINYLURACILS

Z. V. Stepanova, G. G. Skvortsova,*
V. K. Voronov, and A. V. Afonin

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.

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 567-568, April, 1986. Original article submitted July 15, 1985.

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REACTION OF 8-BROMO-3-METHYLXANTHINE WITH AMINES IN DMFA

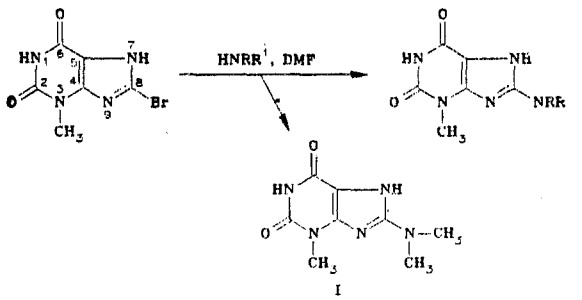
N. I. Romanenko, N. A. Klyuev, B. A. Priimenko, N. V. Fedulova, and A. N. Stepanov

UDC 547.857.4:07:543.51

It is known [1, 2] that 8-aminoxanthines are formed when the corresponding 8-halo derivatives are heated with amines in ethanol under pressure or in methoxyethanol.

We studied the reaction of 8-bromo-3-methylxanthine with primary and secondary amines in DMFA. Instead of the expected 8-alkyl, dialkyl, cycloalkylamino-substituted 3-methylxanthines, only one compound, 3-methyl-8-N,N-dimethylaminoxanthine (I) was obtained and identified in all cases.

As far as we know from the literature, no similar reactions, in which DMFA would compete with strong nucleophiles in the nucleophilic substitution reactions are known. It is probable that the mechanism of this reaction is as follows. A proton is split from the $N_{(7)}$ atom by the action of amine. The 8-bromo-3-methylxanthinylium anion formed adds to the carbonyl atom of DMFA with simultaneous elimination of dimethylamide anion, which then plays the role of nucleophile. Further, with the participation of an excess of the amine, a further elimination of the N_7-formyl group takes place.



I

A mixture of 0.1 mole of 8-bromo-3-methylxanthine, 0.3 mole of benzylamine, cyclohexylamine, monoethanolamine, n-hexylamine, N-benzylaminoethanol, or diethanolamine is boiled in 100 ml of DMFA for 2-4 h. The mixture is cooled, washed with hot water, ammonia, water, and dried. The precipitate is crystallized from glacial acetic acid. The yield of 3-methyl-8-N,N-dimethylaminoxanthine (I) is 60-80%, mp >330°C. PMR spectrum (DMSO, standard TMS): 3.015 [s, 6H, $N(CH_3)_2$], 3.297 (s, 3H, 3-CH_3), 10.352 (s, 1H, 7-H), 11.360 ppm (s, 1H, 1-H). Mass spectrum (m/z): 210 (10), 209 (100) $[M]^+$ (determined 209.0878, calculated 209.0193 for $C_8H_{11}N_5O_2$), 194 (61) $[M - CH_3]^+$, 180 (49) $[M - NCH_3]^+$ (determined 180.0627, calculated 180.0647 for $C_7H_8N_4O_2$), 166 (13) $[M - C_2H_5N]^+$ and $[M - HNCO]^+$ (Ph) (determined 166.0501 and 166.0830, calculated 166.0491 and 166.0854 for $C_6H_6N_4O_2$ and $C_7H_{10}N_4O$, respectively), 165 (15) $[Ph - H]^+$ (determined 165.0770, calculated 165.0776 for $C_7H_9N_4O$), 138 (18) $[Ph - CO]^+$, 137 (40) $[(Ph - H) - CO]^+$, 124 (39) $[(Ph - CO - CH_3]^+$, 111 (10), 109 (14); 104.5 (12) $[M]^{2+}$, 68 (51), 53 (49).

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