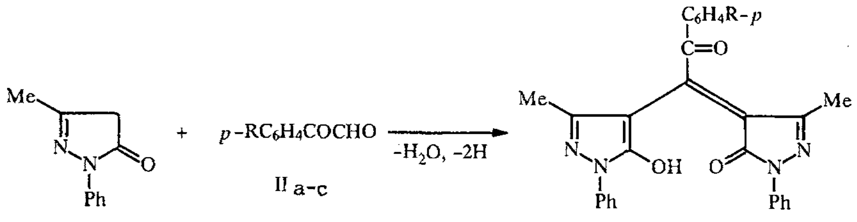

II, IIIa R=H, b R=NO_2, c R=OH

Compound IIIa. This compound had mp 178°C [benzene—hexane (1:4)]. IR spectrum (CCl_4): 1693, 1513, 1500, 1320 cm^{-1}. PMR spectrum ($CDCl_3$): 1.942 (3H, s, CH_3), 1.956 (3H, s, CH_3), 7.3-8.0 (15H, m, aromatic H), 13.87 ppm (1H, s, OH). M^+ 462 (M_{calc} 462). The yield was 73%.

Compound IIIb. This compound had mp 232°C (acetone). IR spectrum (CCl_4): 1693, 1513, 1502, 1348, 1328 cm^{-1}. PMR spectrum ($CDCl_3$): 1.917 (6H, s, CH_3), 7.24-7.34 (14H, m, aromatic H), 13.65 ppm (1H, s, OH). M^+ 507 (M_{calc} 507). The yield was 75%.

Compound IIIc. This compound had mp 225°C ($CHCl_3$). IR spectrum (CCl_4): 3593, 1680, 1500, 1320 cm^{-1}. PMR spectrum ($CDCl_3$): 1.959 (8H, s, CH_3), 7.00-7.9 (15H, m, aromatic H + p-OH), 13.70 ppm (1H, s, OH). M^+ 478 (M_{calc} 478). The yield was 75%.

The results of elementary analysis were in agreement with the calculated values.

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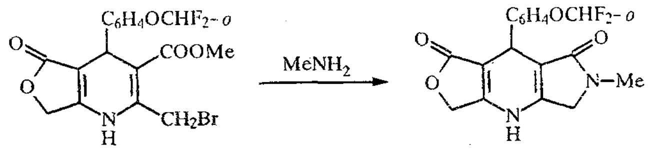
FORMATION OF A NEW HETEROCYCLIC SYSTEM — FURO[3,4-b]PYRROLO[3,4-E]PYRIDINE

I. P. Skrastin'sh, V. V. Kastron,
and G. Ya. Dubur

Various derivatives of polynuclear heterocycles have been obtained as a result of chemical transformations of 1,4-dihydropyridines: furo[3,4-b]pyridines [1-3], difuro[3,4-b;3,4-e]pyridines [4], and pyrrolo[3,4-b]pyridines [5, 6]. However, compounds that contain both a lactam ring and a lactone ring were unknown among 1,4-dihydropyridine derivatives.

To study the possibility of the synthesis of a new heterocyclic system we carried out the reaction of 2-bromomethyl-1,4,5,7-tetrahydro-4-(2-difluoromethoxyphenyl)-3-(methoxycarbonyl)furo[3,4-b]pyridine (I) with methylamine.



I　　II

Substitution and subsequent heterocyclization to give a new, previously undescribed, heterocyclic system — furo[3,4-b]pyrrolo[3,4-e]pyridine II — occur as a result of the reaction.

Institute of Organic Synthesis of the Latvian Academy of Sciences, Riga 226006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 570-571, April, 1992. Original article submitted November 25, 1991.

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2,3,4,6,7,8-Hexahydro-7-(2-difluoromethoxyphenyl)-6,8-dioxofuro[3,4-b]pyrrolo[3,4-e]pyridine (II). A solution of 1.75 g (0.04 mole) of tetrahydrofuro[3,4-b]pyridine I in 20 ml of ethanol and 6.25 ml (0.05 mole) of a 30% aqueous solution of methylamine was stirred for 4 h, after which 50 ml of water was added, and the precipitate was crystallized from acetone to give 0.3 g (22%) of colorless crystals of II with mp 269-271°C. UV spectrum, λ_{max} ($\log \varepsilon$): 212 (4.22), 331 nm (3.88). IR spectrum: 1657, 1686, 1760, 3120, 3182 cm^{-1}. PMR spectrum ($CDCl_3$): δ 2.69 (3H, s, $N-CH_3$), 3.98 (2H, s, CH_2N), 4.81 (3H, s, CH_2O and 4-H), 7.14 (1H, t, J = 75 Hz, CHF_2), 6.9-7.3 ppm (5H, m, Ar—H and NH). Mass spectrum, m/z: 348 $[M]^+$, 320 $[M - CO]^+$, 284, 279 $[320 - CH_3CN]^+$, 272, 268, 251 $[279 - CO]^+$, 208 $[M - C_6H_4OCHF_2 + 3H]^+$, 205 $[M - C_6H_4OCHF_2]^+$, 176 $[205 - CHO]^+$.

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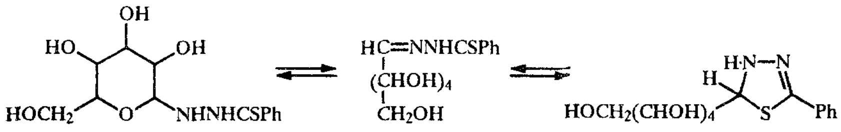
THIOBENZOYLHYDRAZINOPYRANOSIDE—1,3,4-THIADIAZOLINE RING-CHAIN EQUILIBRIUM FOR GLUCOSE THIOBENZOYLHYDRAZONE

V. V. Alekseev and K. N. Zelenin

Arabinose thiobenzoylhydrazone [1], the structure of which has not been studied, is the only known monose (monosaccharide) thiobenzoylhydrazone. If one takes into account the tendency of aldehyde thiobenzoylhydrazones to exist in the 1,3,4-thiadiazoline form [2] and the tendency of aldose hydrazones to exist in the pyranose form [3-5], a ring-chain equilibrium between them is likely for such substances.

It was found that thiobenzoylhydrazone I, which we synthesized in 80% yield (by refluxing thiobenzhydrazide with mannose in methanol) exists in solution in d_6-DMSO in the form of a tautomeric mixture of linear form A (signals of a C=S carbon atom at 183.0 ppm and of a C=N carbon atom at 144.8 ppm) and a cyclic tautomer, which can, with confidence, be identified as 1,3,4-thiadiazoline derivative B, since its spectrum contains signals at 143.0 and 77.6 ppm of the $C_{(2)}$ and $C_{(5)}$ atoms of this ring [2].



C A B

I glucose II mannose

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