SYNTHESIS OF 4,5-'ANHYDRO-3-(2,3-O-ISOPROPYLIDENE-β-D-RIBOFURANOSYL)-4-HYDROXYHEXAHYDROPYRIMIDINE-2-THIONE AND ITS CONVERSIONS IN DILUTE ACETIC ACID

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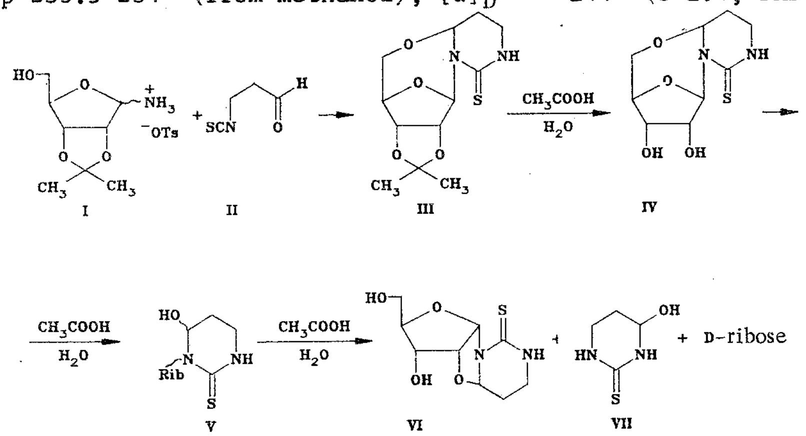
The reaction of ammonia or primary amines with β-isothiocyanatocarbonyl compounds is a convenient method for the synthesis of 4-hydroxyhexahydropyrimidine-2-thiones [1, 2]. In order to broaden the use of this reaction in the synthesis of N-glycosides of hydrogenated pyrimidine-2-thiones in [3], we found that the reaction of 2,3-O-isopropylideneribofuranosylammonium p-toluenesulfonate (I) with 4-isothiocyanato-4-methyl-2- pentanone in pyridine gives a mixture of isomeric 3-(2,3-O-isopropylidene-β-D-ribofuranosyl)-4,6,6-trimethyl-1,2,-3,6-tetrahydropyrimidine-2-thione and 3-(2,3-O-isopropylidene-β-D-ribofuranosyl)-4-methylene-6,6-dimethylhexahydropyrimidine-2-thione in low yield (up to 10%).

The present communication studied the reaction of I with 3-isothiocyanatopropanal (II) in chloroform in the presence of triethylamine or in pyridine at 0°. 4,5'-Anhydro-3-(2,3-O-isopropylidene-β-D-ribofuranosyl)-4-hydroxyhexahydropyrimidine-2-thione (III) is formed in up to 80% yield, mp 233.5-234° (from methanol), $[\alpha]_D^{20}$ − 144° (c 1.4, DMSO).



When a solution of III in dilute (25% by vol.) acetic acid is heated at 97° for 5 h, the main product is 4,2'-anhydro-3-(α-D-ribofuranosyl)-4-hydroxyhexahydropyrimidine-2-thione (IV) in up to 60% yield, mp 222,223° with decomposition (from methanol), $[\alpha]_D^{20}$ +222.4° (c 1.2, DMSO). 4-Hydroxyhexahydropyrimidine-2-thione and D-ribose are also formed in ∿10%

The reaction dynamics were studied by TLC and PMR spectrospcopy, and the intermediate products were separated by column chromatography. We showed that the first intermediate formed from III is 4,5-anhydro-3-(β-D-ribofuranosyl)-4-hydroxyhexahydropyrimidine-2 thione(IV). Scission of the 4,5'-ether bridge of IV gives 3-(D-ribosyl)-4-hydroxyhexahydropyrimidine-2-thiones (V); the latter are converted to VI and form the products of glycoside bond scission, viz., VII and D-ribose. Thus, heating the reaction mixture for 1.5 h gives a mixture containing 20 (III), 13 (IV), 8 (V), 47 (VI) and 6% (VII), and D-ribose.

The final compound VI can also be obtained by heating a solution of IV or V in 25% acetic acid.

The structures of III-VII were confirmed by IR, UV, PMR, optical rotatory dispersion, and mass spectra, and by elemental analysis.

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NEW SYNTHESIS OF 2-THIOXOQUINAZOL-4-ONES

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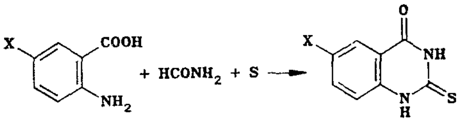
Derivatives of 2-thioxoquinazol-4-ones are usually obtained from anthranilic acids and alkali thiocyanates [1, 2]. We have recently shown that they can be synthesized by the fusion of quinazol-4-ones with sulfur [3]. But in the latter case the intermediate synthesis of quinazol-4-ones is required.

We find that 2-thioxaquinazolones Ia,b form in one step when anthranilic acid or its 5-methyl derivative are heated with formamide and sulfur.



I a X=H; b X=CH_3

The reaction is carried out at 100-120° for 1 h, then at 220-230° for another hour. It proceeds via the intermediate formation of quinazol-4-ones. Thus, when 5-methylanthranilic acid was heated with formamide and sulfur at 200-210° for 20 min, 6-methylquinazol-4-one (91%) and 6-methyl-2-thioxoquinazol-4-one (9%) were separated from the reaction mixture. Further heating of the reaction mixture gave complete conversion to 6-methyl-thioxoquinazol-4-one, Ib.

The reaction is probably of a general nature and is applicable to the synthesis of substituted 2-thioxo-quinazol-4-ones.

Compound Ia, yield 76%, R_f 0.23 (Silufol, 9:1 benzene—acetone), mp 298-300° (from alcohol) [4]; Ib, yield 78%, R_f 0.55 (Al_2O_3, 24:1 chloroform—methanol), mp 288-290° (from acetic acid). The structures were confirmed by the IR, PMR, and mass spectra.

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