

starting compound (for DHQ the calculated dipole moment is 0.7954 D and 2.0078 D for the free radical; for the THQ molecule it is 1.0049, for the free radical it is 2.1541 D). This increase should appear as a large Stokes shift in the fluorescence of the aminic free radicals analogous to that found in [9].

The general increase in the basic properties of the radicals of DHQ and THQ compared to the starting amines in our opinion is caused by the fact that in the free radical the degree of charge transfer from the amino group to the benzene ring is decreased which leads to excess charge on the N atom.

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CONCLUSION

The pK's of short-lived aminic free radicals from 1,2-dihydro- and 1,2,3,4-tetrahydroquinolines were determined. It was shown that the free radicals are stronger bases than the starting amines.

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NEW METHOD OF SYNTHESIS OF SUBSTITUTED 2-PYRIDONES

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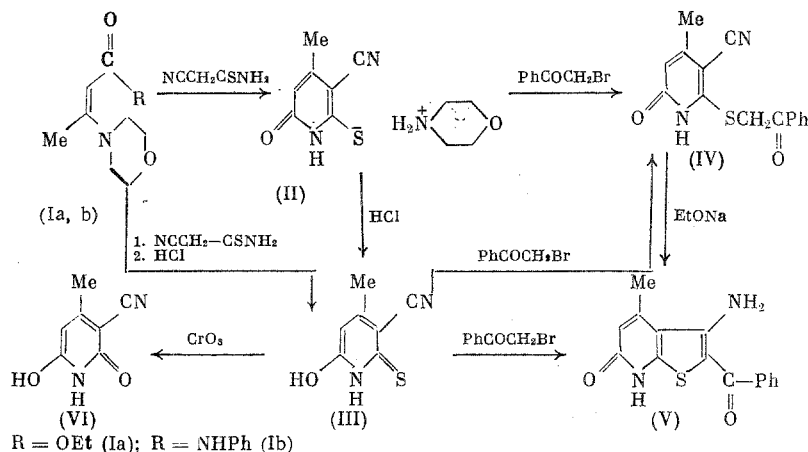
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It is known that condensation of acetoacetic ester with cyanothioacetamide in a mixture of 1-hexanol and pyridine in the presence of β -diethylaminoethanol at 160° results in the formation of 6-hydroxy-4-methyl-3-cyanopyridin-2[1H]-thione (III) [1].

We have shown that β -morpholinoethylcrotonate (Ia) and the anilide (Ib) are more reactive in this reaction in comparison with acetoacetic ester. Thus reaction of the enamine (Ia) or the anilide (Ib) with cyanothioacetamide is autocatalytic and readily occurs in an alcohol medium at ~ 20°. In this case the morpholine salt of 6-oxo-4-methyl-3-cyanopyridine-2[1H]-thiol (II) is formed in high yield, which under the action of hydrochloric acid is smoothly converted into the thione (III), identical with a known sample [1]. Compound (III) was obtained in quantitative yield when the reagents were condensed in aqueous medium and the mixture subsequently acidified with hydrochloric acid.

The thione (III) in the presence of bases and the salt (II) directly are alkylated by phenacyl bromide to 4-methyl-2-phenacylthio-3-cyanopyridone-6[1H] (IV), which under the action of sodium ethylate is cyclized to 3-amino-2-benzoyl-4-methyl-6-oxo-[7H]-thieno[2,3-b]pyridine (V). The thienopyridine (V) can also be prepared in a single stage from the thione (III) by leaving out the pyridone (IV) separation stage. In addition, the struc-

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ture of compounds (II) and (III) was confirmed by their oxidation [2] with chromic anhydride to the corresponding 6-hydroxy-4-methyl-3-cyanopyridone-2-[1H] (VI), identical in properties with those described earlier for (VI) in [3].

The structures of all the isolated products were concordant with the data of the physicochemical studies and the elemental analysis. At the same time the IR and PMR spectral data for compounds (IV) and (V) indicated the latter to have the pyridone structure. Thus their IR spectra exhibited the characteristic absorption band of the amide group at 1638 and 1648 cm^{-1} respectively. The PMR spectra showed the characteristic presence of signals due to the NH group in the region δ 11.78 and 12.29 ppm and of the CH group of the pyridine nucleus in the region δ 6.33 and 6.16 ppm respectively.

EXPERIMENTAL

IR spectra of compounds in KBr tablets were recorded on a UR-20 spectrophotometer. The PMR spectra were recorded on a Varian FT-80A (80 MHz) spectrometer using solutions in DMSO- d_6 and internal standard TMS. Monitoring the course of the reactions and the homogeneity of the compounds obtained was carried out by means of TLC on Silufol UV-25 sheets using the systems acetone-hexane (3:5) and acetone-benzene (1:3).

Morpholine Salt of 6-Oxo-4-methyl-3-cyanopyridine-2[1H]thiol (II). a) A mixture of 20 mmole (Ia) and 20 mmole of cyanothioacetamide in 30 ml ethanol were stirred for 5 h at 20°C. The precipitate was filtered off and washed with ethanol and hexane. After recrystallization from ethanol (II) was obtained in 87% yield, mp 225-228° (with dec.). IR spectrum (KBr, ν cm^{-1}): 2203 (CN), 1643 (CONH). PMR spectrum (DMSO- d_6 , δ , ppm): 1.98 s (CH₃), 3.05 m (4H, CH₂NCH₂), 3.70 m (4H, CH₂OCH₂), 5.36 s (CH), 10.30 s (NH). Found: C 52.07; H 5.76; N 16.43; S 12.61%. C₁₁H₁₅N₃O₂S. Calculated: C 52.16; H 5.97; N 16.59; S 12.66%.

b) A mixture of 10 mmole (Ib) and 10 mmole cyanothioacetamide in 20 ml ethanol was stirred for 24 h at 20°. The yield of (II) was 67%. The compounds obtained by methods a) and b) had identical IR spectra.

6-Hydroxy-4-methyl-3-cyanopyridin-2-thione (III). a) A mixture of 10 mmole (Ia) and 10 mmole cyanothioacetamide in 20 ml water was stirred for 5 h at 20°C. After acidification with 2 ml of conc. HCl the precipitate was filtered off and successively washed with water, ethanol, and hexane. The yield of compound (III) was quantitative.

b) By this method (III) was obtained by acidification of the morpholine salt (II) with conc. HCl. The compounds obtained by the methods a) and b) were identical with (III) described earlier [1].

6-Hydroxy-4-methyl-3-cyanopyridin-2-one (VI). To a suspension of 2 mmole (III) in 30 ml AcOH was added a solution of 7 mmole CrO₃ in 4 ml water and the mixture heated at boiling for 2 h. After cooling the reaction mixture water was added and the precipitate separated. Yield of (VI) 57%, mp 298-300°C; the compound was identical to (VI) obtained previously [2].

4-Methyl-3-phenacylthio-3-cyanopyridin-6-one (IV). a) To a suspension of 10 mmole (II) in 30-35 ml dry benzene or abs. alcohol at 20°C was added 10 mmole of phenacyl bromide. The reaction mixture was stirred for 5-6 h. The yield of (IV) after recrystallization from ethanol was 89%, mp 198-200°C.

b) To a solution of 10 mmole (III) in 20 ml DMF while stirring was added successively 5.6 ml of a 10% KOH solution and 10 mmole phenacyl bromide. The reaction mixture was stirred 1 h at 20°C, 10 ml of water added and the precipitate filtered off. Yield of (IV) by this method was 93%.

The compounds obtained by methods a) and b) had identical IR and PMR spectra. IR spectrum (KBr, ν , cm^{-1}): 2218 (CN), 1693 (CO), 1638 (CONH). PMR spectrum (DMSO- d_6 , δ , ppm): 2.30 s (CH_3), 4.89 s (CH_2), 6.33 s (CH), 7.3-8.1 m (C_6H_5), 11.78 s (NH). Found: C 63.23; H 4.17; N 9.71; S 11.12%. $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$. Calculated: C 63.36; H 4.26; N 9.85; S 11.28%.

3-Amino-2-benzoyl-4-methyl-6-oxo-7H-thieno[2,3-b]pyridine (V). To a solution of sodium alcoholate, prepared from 7 mmole sodium and 15 ml ethanol, was added 3.5 mmole of (IV). The reaction mixture was heated at boiling for 3 h with stirring, filtered and then the filtrate acidified with a 10% solution of HCl to pH 5-6. The precipitate was separated and recrystallized from glacial acetic acid. Compound (V) was obtained in 80% yield, mp 299-301°C. IR spectrum (KBr, ν , cm^{-1}): 3460, 3305 (NH_2), 1648 (CONH), 1588 (COC_6H_5). PMR spectrum (DMSO- d_6 , δ , ppm): 2.55 s (CH_3), 6.16 s (CH), 7.50 m (C_6H_5), 7.88 s (NH_2), 12.29 s (NH). Found: C 63.22; H 4.10; N 9.74; S 11.20%. $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$. Calculated: C 63.36; H 4.26; N 9.85; S 11.28%.

CONCLUSIONS

1. A new method of synthesis of 6-hydroxy-4-methyl-3-cyanopyridin-2[1H]thione has been developed which consists of the reaction of β -morpholinoethylcrotonate or its corresponding anilide with cyanothioacetamide.

2. 6-Hydroxy-4-methyl-3-cyanopyridin-2[1H]thione is selectively alkylated at the sulfur atom.

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CONFORMATIONAL FLEXIBILITY OF THE TWELVE-MEMBERED SILOXANE RING

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It is known that cycloalkanes of moderate size ($n = 6-10$) are characterized by conformations similar in energy [1, 2]. As shown by calculation and experimental investigations [3, 4], a conformation with two parallel planar transoid chains, containing 4-5-unit terminal segments is usually realized in large cycloalkanes ($n > 20$). The favorability of such a conformation with respect to energy is understandable, since the maximum van der Waals interaction is realized with the parallel arrangement of the aliphatic chains.

Cyclic siloxanes of medium size are also characterized by a large variety of conformers. However, they differ less in energy than in the case of cycloalkanes, as was demonstrated for the case of the tetrasiloxane ring [5]. The conformations of siloxane molecules with large rings, which have not been studied in detail, are evidently characterized by the same features as for cycloalkanes, i.e., the presence of two parallel chains linked by the terminal fragments. The only difference between the cyclosiloxanes and cycloalkanes is the fact that there is only one type of van der Waals interaction (disregarding substituents) in the case of the aliphatic chains, while there are three types in the case of siloxane chains with alternating Si and O atoms.

In the present work we studied the possible conformational changes in the siloxane rings during the transition from medium to large rings for the case of the twelve-membered siloxane ring of 2,8-dihydroxy-2,4,-

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