6-CH_2), 1.80 (4H, m, 3- and 5-CH_2), and 1.30 ppm (6H, s, 2-CH_3). Found: C 53.8; H 6.1; N 10.0; S 12.0%; M^+ 268. $C_{12}H_{16}N_2O_3S$. Calculated: C 53.7; H 6.0; N 10.4; S 11.9%; M 268.

2-Amino-4-hydroxy-5-(2,2-dimethyltetrahydro-4-pyranoyl)pyrimidine (IX). Similarly, the reaction of 1.4 g (5 mmole) of ester II, 0.5 g (5 mmole) of guanidine hydrochloride, and a solution of sodium ethoxide gave 1.1 g (89%) of IX with mp 256-257°C and R_f 0.44. IR spectrum (in mineral oil): 1600 (aromatic pyrimidine ring), 1665 (ring C=O), 1680 (keto C=O), and 3200-3300 cm^{-1} (NH, NH_2). PMR spectrum (in d_5-pyridine): 11.60 (2H, s, NH_2), 8.00 (1H, s, N=CH), 4.50 (1H, m, 4-CH), 3.80 (2H, m, 6-CH_2), 1.80 (4H, m, 3- and 5-CH_2), and 1.30 ppm (6H, s, 2-CH_3). Found: C 57.6; H 6.7; N 16.6%; M^+ 251. $C_{12}H_{17}N_3O_3$. Calculated: C 57.4; H 6.8; N 16.7%; M 251.

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O-ETHYLVALEROLACTONIUM TETRAFLUOROBORATE AND VALEROLACTONE DIETHYLACETAL IN THE SYNTHESIS OF CONDENSED PYRANS

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A pyrano[2,3-b]quinoline derivative was obtained by the reaction of O-ethylvalerolactonium tetrafluoroborate with ethyl anthranilate and subsequent cyclization of the intermediate imido ester. A number of derivatives of pyrano[3,2-c]pyridine and pyrano[2,3-d]pyrimidine derivatives were synthesized on the basis of valerolactone diethylacetal and α-dimethylaminomethylenevalerolactone diethylacetal.

In [1-4] we published data from a study of the properties of previously little-investigated activated lactones. These studies dealt only with butyrolactone derivatives. The aim of the present research was to investigate the properties and transformations of derivatives of a representative of a homologous series of lactones, viz., valerolactone.

Valerolactone (I) was synthesized from δ-chlorovaleric acid by the method in [5]. Activation of the lactone carbonyl group was realized by alkylation of it with triethyloxonium tetrafluoroborate to give O-ethyllactonium tetrafluoroborate (II). In [1, 2] it was shown that the complex of butyrolactone with triethyloxonium tetrafluoroborate reacts with substituted anilines to give the corresponding imido ester salts, from which one can obtain condensed three-ring compounds. Complex II also reacts smoothly with ethyl anthranilate to give an imido ester tetrafluoroborate, which is converted to the base by treatment with triethylamine. Imido ester III, without isolation in the individual state, undergoes intramolecular cyclization when it is refluxed in an alcohol solution of sodium ethoxide. The resulting sodium derivative of pyrano[2,3-b]-4-quinolone is treated with hydrochloric acid solution, and 5-oxo-2H,3,4,5,10-tetrahydropyrano[2,3-b]quinoline (IV) is isolated.

Valerolactone diethylacetal (V), which was mentioned only in [6] in connection with a study of the hydrolysis of cyclic ortho esters, was obtained by exchange decomposition of complex II with a solution of sodium ethoxide. Like butyrolactone acetal, it can react with compounds that have active methylene groups. The reactions of acetal V with cyanoacetamide and cyanoacetic ester take place by heating the reaction mixtures to 130-150°C with removal

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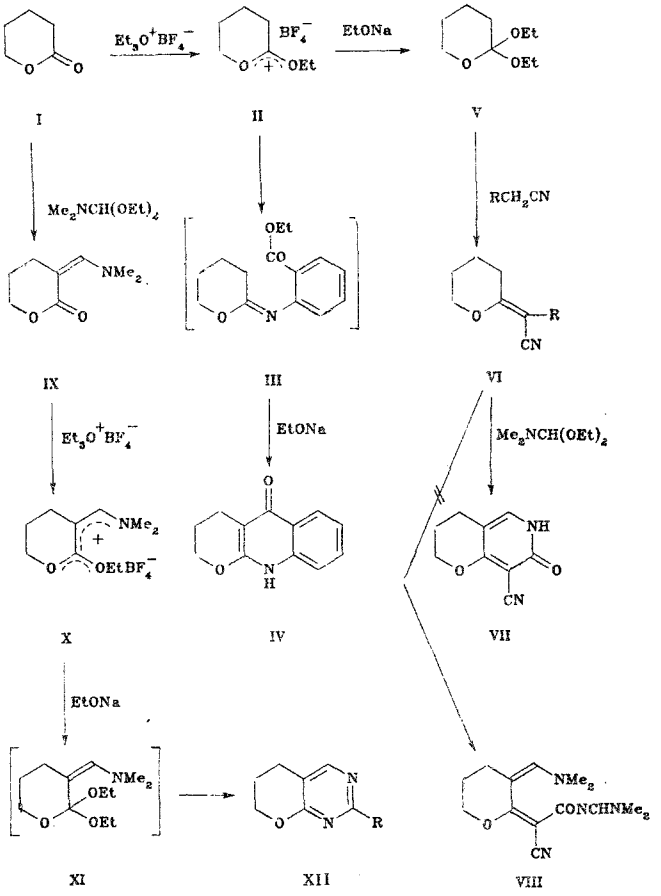
of the liberated alcohol by distillation. However, the use of a catalyst (in contrast to similar reactions of ortho esters [7]) is not required. As a result, we obtained 2-methylenepyrans VI.

Using amide VIb, one can also readily obtain condensed oxazaheterocycles. The reaction of amide VIb with dimethylformamide acetal leads to the formation of pyrano[3,2-c]pyridine (VII). In contrast to the tetrahydrofuran derivative, for which a dieneaminoacylamidine of the VIII type was obtained in a similar reaction, two-ring compound VII is formed in this reaction. This difference in the reactions can be explained by the relative ease of formation of a pyridine ring condensed with a six-membered ring as compared with the same process for a five-membered ring [8].

To obtain a lactone acetal that is more reactive with respect to nucleophilic reagents, i.e., an acetal for which one can imagine an ambident cation with a higher degree of charge delocalization, enaminolactone IX was synthesized by the reaction of valerolactone with DMF acetal. The alkylation of lactone IX with triethyloxonium tetrafluoroborate gave the corresponding tetrafluoroborate complex X; the reaction is exothermic. Acetal XI, which, because of its instability, was used without purification in subsequent reactions, we obtained from complex X. Pyrano[2,3-d]pyrimidine derivatives XII were synthesized by the reaction of acetal XI with guanidine and dicyandiamide.



VI a R=CO_2Et, b R=$CONH_2$; XII a R=NH_2, b R=NHCN

EXPERIMENTAL

5-Oxo-2H,3,4,5,10-tetrahydropyrano[2,3-b]quinoline (IV). A 15-ml sample of valerolactone was added to 28 g (147.5 mmole) of triethyloxonium tetrafluoroborate, and the mixture was maintained at room temperature for 24 h in a refrigerator. The upper layer was decanted, and complex II, which began to solidify, was washed with anhydrous ether. A solution of 24.3 g of ethyl anthranilate in 50 ml of anhydrous ether was added to the complex, and the liberated oily salt III was triturated with anhydrous ether. The ether was decanted, and an ether solution of 22 ml of triethylamine was added to the residue. The mixture was tritu-

rated thoroughly until solid triethylamine tetrafluoroborate precipitated, and the precipitate was removed by filtration and washed with anhydrous ether. The filtrate was evaporated *in vacuo*, and the residue was added to a refluxing solution of sodium ethoxide (from 6.7 g of sodium and 150 ml of alcohol). The mixture was refluxed for 3 h, the alcohol was evaporated, and the residue was dissolved in water. The solution was acidified to pH 6 with 1 N HCl, and the resulting precipitate was washed in water with chloroform and removed by filtration to give 8.75 g (29.5%) of IV with mp 274-276°C (from DMF). Found: C 71.5; H 5.4; N 6.8%; M 201. $C_{12}H_{11}NO_2$. Calculated: C 71.6; H 5.5; N 7.0%; M 201.

2-(Ethoxycarbonylcyanomethylene)perhydropyran (VIa). A mixture of 9 g (50 mmole) of acetal V and 5.8 g (51 mmole) of cyanoacetic ester was refluxed with removal of the alcohol by distillation until the liberation of alcohol ceased completely. The reaction mixture was then cooled, whereupon it began to crystallize to give 9.7 g (quantitative yield) of VIa with mp 87-88°C (from ethyl acetate). IR spectrum: 1570 (C=C), 1710 (C=O), and 2210 cm^{-1} (C≡N). UV spectrum, λ_{max} (log ε): 263 nm (4.26). Found: C 61.5; H 6.9; N 7.2%; M^+ 195. $C_{10}H_{13}NO_3$. Calculated: C 61.5; H 6.7; N 7.2%; M 195.

2-(Carbamidocyanomethylene)perhydropyran (VIb). Compound VIb, with mp 174-175°C (from alcohol), was similarly synthesized in 46.4% yield. IR spectrum: 1560, 1585, 1660 (C=C, NH_2, CO); 2210 (C≡N); 3180, 3260, 3310 cm^{-1} (NH_2). UV spectrum, λ_{max} (log ε): 255 nm (4.19). Found: C 57.9; H 6.5; N 17.1%; M^+ 166. $C_8H_{10}N_2O_2$. Calculated: C 57.8; H 6.0; N 16.9%; M 166.

7-Oxo-8-cyano-2H,3,4,6,7-tetrahydropyrano[3,2-d]pyridine (VII). A mixture of 1.8 g (10.8 mmole) of VIb, 5 ml of DMF acetal, and 20 ml of anhydrous toluene was refluxed for 2 h, after which it was cooled, and the resulting precipitate was removed by filtration to give 0.9 g (47.2%) of pyranopyridine VII with mp 310-311°C (from water). IR spectrum: 1550 (C=C), 1645 (C=O), and 2212 cm^{-1} (C≡N). UV spectrum, λ_{max} (log ε): 225 (4.46), 260 (3.51), 267 (3.46) shoulder, and 320 nm (3.83). Found: C 61.5; H 4.6; N 15.9%; M^+ 176. $C_9H_8N_2O_2$. Calculated: C 61.4; H 4.6; N 15.9%; M 176.

2-Oxo-3-dimethylaminomethyleneperhydropyran (IX). A) A mixture of 10 g (0.1 mole) of valerolactone and 20 g of DMF acetal was heated in a bomb at 160-180°C for 7 h, after which it was distilled with selection of the fraction with bp 160-180°C (3 mm) to give 7.9 g (51%) of IX with bp 192-193°C (7 mm). IR spectrum: 1575 (C=C) and 1680 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 302 nm (4.30). Found: C 61.8; H 8.5; N 9.3%; M^+ 155. $C_8H_{13}NO_2$. Calculated: C 61.9; H 8.4; N 9.0%; M 155.

B) A mixture of 4.7 g (47 mmole) of valerolactone and 6.9 g (47.3 mmole) of DMF aminal was heated at 120°C for 4 h, after which it was evaporated *in vacuo*, and the residue was distilled with collection of the fraction with bp 172-187°C (3 mm) to give 6.53 g (89%) of IX, which began to crystallize on standing.

2-Ethoxy-3-dimethylaminoperhydropyranium Tetrafluoroborate (X). An 11.3-g sample of triethyloxonium tetrafluoroborate was added to 9.2 g (59.3 mmole) of IX in 50 ml of anhydrous benzene, and the mixture was maintained at room temperature for 2 h and stored in a refrigerator for 2 days. The semicrystalline mass was filtered, and the solid material was washed with anhydrous ether and dried to give 9 g of X. The upper layer of the filtrate was decanted, and the lower layer was triturated with isopropyl alcohol. The resulting precipitate was removed by filtration, washed with anhydrous ether, and dried to give 2.05 g of X for an overall yield of 11.05 g (68.7%) of a product with mp 107-108°C (from alcohol). IR spectrum: 1525 (C=C) and 1635 cm^{-1} ($C=N^+$). UV spectrum, λ_{max} (log ε): 312 nm (4.48). Found: C 44.3; H 6.4; N 5.1%. $C_{10}H_{18}BF_4NO_2$. Calculated: C 44.3; H 6.6; N 5.2%.

7-Amino-2H,3,4-dihydropyrano[2,3-d]pyrimidine (XIIa). A 2-g sample of guanidine hydrochloride and 2.8 g (10 mmole) of complex X were added to a solution of sodium ethoxide (from 1 g of sodium and 30 ml of alcohol), after which the mixture was refluxed for 3 h, the alcohol was evaporated *in vacuo*, and the residue was dissolved in water. The aqueous solution was extracted with chloroform, the extract was dried with sodium sulfate and evaporated, and the residue was triturated with ethyl acetate to give 0.74 g (49%) of XIIa with mp > 200°C (sublimation, from water). IR spectrum: 1560, 1615 (C=C); 1670 (C=N); 3120, 3295 cm^{-1} (NH_2). Found: C 55.9; H 5.5; N 28.3%; M^+ 151. $C_7H_9N_3O$. Calculated: C 55.6; H 6.0; N 27.8%; M 151.

7-Cyanoamino-2H,3,4-dihydropyrano[2,3-d]pyrimidine (XIIb). A 0.84-g (10 mmole) sample of N-cyanoguanidine and 2.8 g (10 mmole) of complex X were added to a solution of sodium ethoxide (from 0.5 g of sodium and 30 ml of alcohol), and the mixture was refluxed for 3 h. The alcohol was evaporated, the residue was dissolved in water, and the aqueous solution was acidified to pH 7 with 1 N HCl. The resulting precipitate was removed by filtration, washed with alcohol, and dried to give 0.77 g (43.8%) of XIIb with mp > 320°C (from DMF). IR spectrum: 1580 (C=C), 1645 (C=N), 2150 (C≡N), and 3010 cm^{-1} (NH). Found: C 54.3; H 4.6; N 32.5%; M^+ 176. $C_8H_8N_4O$. Calculated: C 54.6; H 4.6; N 31.8%; M 176.

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POLYARALKYLATION OF PRIMARY AROMATIC AMINES WITH 6-HYDROXY-2,4-DIMETHYL-1,3-BENZODIOXANE

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6-Hydroxy-2,4-dimethyl-1,3-benzodioxane is cleaved with opening of the 1,3-dioxane ring in a mixture of acetic and hydrochloric acids. The resulting hydroquinone-containing fragments N-aralkylate the primary amines (aminoanthraquinone, p-nitroaniline, and p-aminoazobenzene) which are added to the reaction mixture to give the corresponding N-(polyethylidenehydroquinone)arylamines.

Azo and anthraquinone dyes that contain hydroquinone residues have been used as developers for color photography [1-4]. The existing methods for the preparation of such dye-developers are usually multistep processes. In order to develop a method for the introduction of hydroquinone residues into aromatic compounds we studied the reaction of primary aromatic amines with 6-hydroxy-2,4-dimethyl-1,3-benzodioxane (I), which can be readily obtained from hydroquinone and acetaldehyde [5]. Bearing in mind the ability of 1,3-benzodioxanes to undergo cleavage to give fragments that are capable of aralkylating alcohols and thio alcohols [6, 7], we assumed that benzodioxane I would be a suitable reagent for the introduction of a hydroquinone residue into arylamine molecules. The amines that are usually employed in the synthesis of dyes, viz., p-nitroaniline (II), 1-aminoanthraquinone (III), 1,4-diaminoanthraquinone (IV), 1,4-diamino-5,8-dihydroxyanthraquinone (V), and p-aminoazobenzene (VI), were used as the starting compounds.

We found that benzodioxane I is cleaved with opening of the 1,3-dioxane ring in solution in acetic acid under the influence of concentrated hydrochloric acid and that the cleavage products react with the arylamine added to the reaction mixture to give several reaction products. However, by using a sufficiently large amount of hydrochloric acid (more than 20 moles per mole of benzodioxane I) one can direct the reaction to give primarily an N-substituted arylamine containing hydroquinone residues in the side chain. Compounds of this type were obtained in the reaction of benzodioxane I with all of the amines listed above (II-VI). On

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