stance vigorously liberates iodine from a solution of sodium iodide in acetic acid. Found, %: C 70.17, 70.00; H 10.02, 10.26; N 6.42, 6.47. Calculated for $C_{13}H_{21}NO_2$, %: C 69.96; H 9.42; N 6.30. The somewhat high analytical results are possibly due to the presence of a small amount of **III** in the hydroperoxide. The hydroperoxide can be stored at 0° C for 10 days with no change in the melting point.

12-Hydroxy-Δ^{10}-dodecahydroacridine (III). A mixture of 2.8 g of the hydroperoxide **II**, 50 ml of ether, 50 ml of 1N KOH solution, and 6 g of sodium hydrosulfite was stirred at room temperature until the qualitative reaction for hydroperoxide was negative. The reaction product was separated off, washed with water, and dried. Yield 0.97 g (37.5%). Rods, soluble in acetic acid and dioxane, sparingly soluble in ethanol and benzene, insoluble in water, petroleum ether, and diethyl ether. Mp 191–192° C (from aqueous ethanol). Found, %: C 75.56, 75.63; H 10.14, 10.06; N 7.03, 6.90. Calculated for $C_{13}H_{21}NO$, %: C 75.40; H 10.14; N 6.76. IR spectrum (in CCl_4), ν, cm^{-1}: 1670 (C=N), 3620 (O–H). Picrate, mp 140–140.5° C (from aqueous ethanol). Found, %: N 12.88, 12.73. Calculated for $C_{13}H_{21}NO \cdot C_6H_3N_3O_7$, %: N 12.83.

5-Azabicyclo[8, 4, 0]tetradecane-6, 11-dione (IV). A mixture of 2.2 g of the hydroperoxide **II**, 20 ml of water, 20 ml of dioxane, and 5 drops of concentrated HCl were stirred at 32–37° C until the almost complete disappearance of the qualitative reaction for hydroperoxide (this required about 10 hr). The mixture was neutralized with a few drops of ammonia solution, and the dioxane and water were distilled off under reduced pressure. The residue was treated with 15 ml of cold acetone, and the rearrangement product was filtered off with suction and then separated from mineral impurities by dissolution in chloroform. This gave 0.9 g (41%) of the product. After two recrystallizations from acetone, mp 146–148° C. Chromatographic purification of the product on a column of Al_2O_3 (elution with chloroform), and subsequent recrystallization from dioxane gave a sample with mp 157.5–158° C. Hexagonal plates, soluble in ethanol, benzene, chloroform, and ethyl acetate, less readily in acetone and dioxane, and sparingly in heptane. Found, %: C 70.23, 70.26; H 10.07, 9.98; N 6.31, 6.38. Calculated for $C_{13}H_{21}NO_2$, %: C 69.96; H 9.42; N 6.30. IR spectrum (in KBr), ν, cm^{-1}: 3280, 3100, 1660, 1580 (–CONHR), 1720 (C=O).

Autoxidation of Δ^{10}-dodecahydroacridine in the absence of a solvent. Compound I (1.4 g) was spread in a thin layer on the bottom of a Petri dish and left in the air for 25 days. The crystalline mass obtained was triturated with heptane, and the crystals were filtered off and washed with hot water. The substance (0.51 g), insoluble in water, was identified as **III**. Evaporation of the aqueous extract yielded 0.63 g of **IV**.

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ANALOGS OF PYRIMIDINE NUCLEOSIDES

IV. The Silyl Method of Obtaining N_1-(α-Tetrahydrofuryl) and N_1-(α-Tetrahydropyranyl) Derivatives of Uracils and 6-Azauracil*

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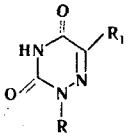
N_1-(α-Tetrahydrofuranyl)- and N_1-(α-tetrahydropyranyl)uracils and the corresponding 6-azauracils have been obtained by the condensation of bistrimethylsilyl derivatives of uracils and 6-azauracils with α-chlorotetrahydrofuran and α-chlorotetrahydropyran. The superiority of the "silyl" method over the "mercury" method used previously has been demonstrated.

We have previously obtained N_1-(α-tetrahydrofuryl)-uracils (**IVa–f**) by the condensation of mercury derivatives of the pyrimidine bases with α-chlorotetrahydrofuran (CTHF) [1], and one of these compounds, **IVc**, is of value as an agent for the treatment of some types of malignant tumors. However, the proposed method of synthesizing compounds IV proved to be unsuitable: the yields were only about 40%, and the process of purification of the end product from traces of mercury proved to be extremely laborious.

In view of the desirability of developing a technologically convenient method, we have studied the possibility of obtaining compounds **IVa–f** by condensing bistri-

*For part III, see [9].

N_1-(α-Tetrahydrofuryl)- and N_1-(α-Tetrahydropyranyl)uracils and -6-Azauracils



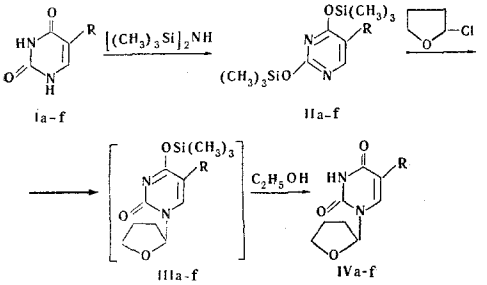
Compound	R	R_1	X	Mp, °C	Empirical formula	Found, %			Calculated, %			UV spectra					
												pH 3—4		pH 7—8		pH 11—12	
						C	H	N	C	H	N	λ_{max}, nm	ε · 10^{-3}	λ_{max}, nm	ε · 10^{-3}	λ_{max}, nm	ε · 10^{-3}
Va	P*	H	CH	186—188	$C_9H_{12}N_2O_3$	55.34	6.44	14.38	55.09	6.16	14.27	256	6.800	256	6.900	255	5.000
Vb	P	CH_3	CH	171—172	$C_{10}H_{14}N_2O_3$	57.35	6.92	13.03	57.13	6.71	13.32	267	8.100	267	7.590	267	6.000
Vc	P	F	CH	172—173	$C_9H_{11}FN_2O_3$	50.64	5.44	13.13	50.46	5.14	13.08	267	8.740	265	6.000	268	6.170
Vd	P	Cl	CH	202—204	$C_9H_{11}ClN_2O_3$	47.29	4.94	13.03	46.80	4.80	12.14	273	10.300	273	9.900	273	7.200
Ve**	P	Br	CH	197—199	$C_9H_{11}BrN_2O_3$	38.93	3.87	10.22	39.25	4.07	10.18	278	12.300	276	11.850	272	9.200
Vf	P	I	CH	184—190	$C_9H_{11}IN_2O_3$	33.62	3.83	8.62	33.53	3.44	8.60	285	8.660	285	6.980	281	5.900
VIa	F	H	N	121—123	$C_7H_9N_3O_3$	45.81	4.80	23.21	45.90	4.95	22.94	262	6.180	261	5.960	255	6.500
VIb	F	CH_3	N	142—143	$C_8H_{11}N_3O_3$	48.48	5.83	22.16	48.72	5.62	21.31	264	6.520	263	6.600	251	7.260
VIc	F	Br	N	211—213	$C_7H_8BrN_3O_3$	32.45	3.61	16.60	32.08	3.08	16.41	277	6.940	276	6.660	265	7.000
VIIa	P	H	N	160—162	$C_8H_{11}N_3O_3$	48.70	5.78	21.31	48.72	5.62	21.31	258	6.940	256	6.500	245	7.270
VIIb	P	CH_3	N	125—128	$C_9H_{13}N_3O_3$	51.27	6.01	19.72	51.17	6.20	19.90	260	6.870	260	7.070	250	7.420
VIIc	P	Br	N	195—197	$C_8H_{10}BrN_3O_3$	34.73	3.81	14.85	34.80	3.65	15.22	275	7.300	270	6.480	257	8.300

*P—tetrahydropyranyl, F—tetrahydrofuryl.

**Found, %: Br 30.33, calculated, %: Br 29.52.

methylsilyl derivatives of the pyrimidine bases (II) with CTHF in a similar manner to the synthesis of some pyrimidine nucleosides [2–4], and we have obtained good results from the preparative point of view in this way. A not unimportant circumstance is the fact that the "silyl method" enables the consumption of CTHF to be halved in comparison with the mercury method [5].

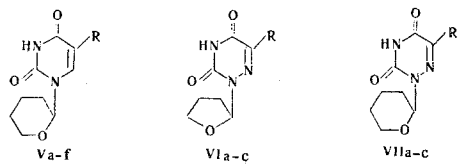
Since the bistrimethylsilyl derivatives of the uracils have the structure II [6], the process of obtaining compounds IV reduces to a sequence of the following stages:



Ia-f IIa-f IIIa-f IVa-f

I-IV a R = H; b R = CH_3; c R = F; d R = Cl; e R = Br; f R = J.

Compounds II can be obtained by the reaction of I both with chlorotrimethylsilane (CTMS) and with hexamethyldisilazane (HMDS); however, the use of the latter has a number of advantages. We used this method of synthesis for obtaining N_1-(α-tetrahydrofuryl) and N_1-(α-tetrahydropyranyl) derivatives of uracils and 6-azauracils (V, VI, and VII). Compounds **Vc, d, VI,** and VII were synthesized for the first time, while we have described compounds **IVb–f** previously [1] and compounds **Va, b, e, f** have been synthesized [7] by the Hilbert-Johnson method. The structure of the compounds obtained was confirmed by a study of the dependence of their UV spectra on the pH of the medium.



Va-f VIa-c VIIa-c

V a R = H; b R = CH_3; c R = F; d R = Cl; e R = Br; f R = J.
VI, VII a R = H; b R = CH_3; c R = Br

Under the given conditions, the 5-substituted uracils and 6-azauracils react more readily than bases having no substituent in position 5, in consequence of which the yields of **Va, VIa,** and **VIIa** were low (~40–30%).

The tetrahydrofuryl derivatives of uracil proved to be less stable to acid hydrolysis than the tetrahydropyranyl derivatives [8], which also explains the greater difficulty of their preparation.

EXPERIMENTAL

The purity of the compounds synthesized was checked by chromatography on "Leningrad slow" paper in the n-C_4H_9OH–CH_3COOH–H_2O (4 : 1 : 5) system.

The UV spectra were taken on a SF-4 spectrophotometer.

N_1-(α-Tetrahydrofuryl)thymine (IVb). A mixture of 12.6 g (0.1 mole) of thymine, 60 ml of HMDS, and 1.2 ml of TMCS was heated at 150–170° C until the thymine had dissolved completely (about 2 hr). The excess of HMDS was distilled off under reduced pressure, and the residue was treated with 20 ml of dry benzene. The mixture was cooled to −20° C in a current of dry nitrogen, and 12.8 g (10.8 ml, 0.12 mole) of CTHF was added at a temperature of −20 to −15° C. The reaction mixture was kept at −20 to −10° C for 4 hr, and then 25 ml of ethanol was added and the crystalline precipitate of **IVb** that deposited was filtered off with suction. Yield: 13.2 g (66%). Mp 182–184° C (from ethanol). Compounds **IVa, c–f** and **VI** were synthesized similarly (table). In those cases where the products obtained were contaminated with the starting materials, additional purification was performed by boiling them with a 10-fold amount of chloroform (**IV**) or carbon tetrachloride (**VIa**). The insoluble part was the corresponding initial base, and the tetrahydrofuryl derivative was isolated from the filtrate.

To purify it from 6-azathymine, **VIb** was boiled with ether, whereupon the 6-azathymine passed into solution. The insoluble residue consisted of **VIb**.

N_1-(α-Tetrahydropyranyl)-5-bromouracil (Ve). A mixture of 3.82 g (0.02 mole) of 5-bromouracil, 15 ml of HMDS, and 0.5 ml of TMGS was heated at 170–180° C until the 5-bromouracil had dissolved completely (about 4 hr). The excess of HMDS was distilled off under reduced pressure, and the residue was cooled to −10° C in a current of dry nitrogen and treated with 3 g (2.5 ml, 0.025 mole) of CTHF. The reaction mixture was stirred at room temperature for 5 hr, and then 20 ml of ethanol was added and it was stirred for another 2 hr. The precipitate of **Ve** that deposited was filtered off with suction. Yield 2.8 g (50.5%). Mp 197–199° C (from ethanol).

Compounds Va–d, f and **VII** were obtained similarly (table). They were freed from traces of the initial base by boiling with chloroform.

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