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ACTIVITY OF METHYL DERIVATIVES OF 5-HYDROXYPYRIMIDINE IN REACTIONS WITH AROMATIC ALDEHYDES

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We established previously that aminomethylation of methyl-substituted 5-hydroxypyrimidines resulted in condensation on the methyl group in the 4(6) position, along with substitution on the pyrimidine ring [1]. We now report the results of another condensation on these compounds.

Reactions with aldehydes, nitroso compounds, and aryl diazonium salts provide a test for the reactivity of protons in CH_3 groups of heterocyclic compounds [2]. Among the most studied reactions of pyrimidines, their condensations with aromatic aldehydes take place on CH_3 groups that are conjugated with a nitrogen. The presence of electron-donating substituents, such as OH, in the ring, makes it difficult or impossible to carry out such reactions, because of the decreased reactivity of the CH_3 protons. For example, 4-hydroxy-6-methylpyrimidine fails to react with benzaldehyde even under drastic conditions [3]. Electron-donating substitutions in the 5-position of the pyrimidine ring also make methyl groups in the 4(6) position unreactive in these condensations [4].

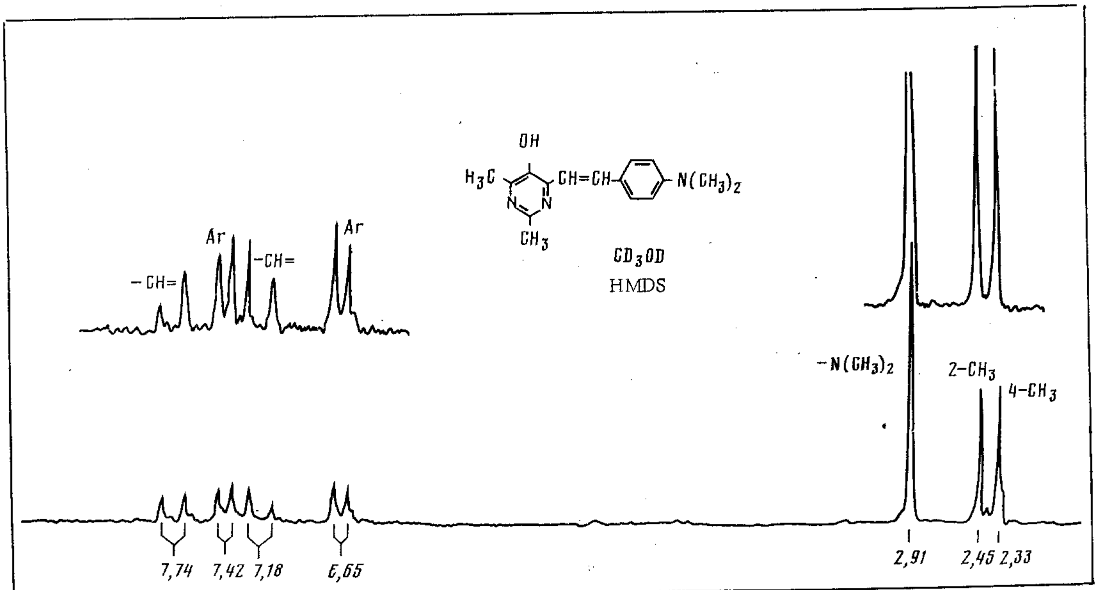

Fig. 1. NMR spectra of 2,4-dimethyl-5-hydroxy-6-(p-dimethylaminostyryl)pyrimidine.

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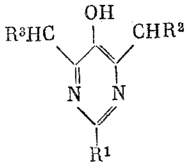
TABLE 1. Yields and Properties of Compounds 

Compound	R^1	R^2	R^3	Yield, † %	mp, °C	Found, % C	Found, % H	Found, % N	Formula	Calculated, % C	Calculated, % H	Calculated, % N
(IV) *	H	H_2	A	24	184–186 alcohol	63,06	5,54	10,81	$C_{13}H_{13}N_2OCl$	62,78	5,26	11,26
(V)	CH_3	H_2	A	16	199–201 alcohol	74,15	6,58	12,22	$C_{14}H_{14}N_2O$	74,31	6,24	12,38
(VI)	H	H_2	B	41	241–243 benzene	70,98	6,35	16,52	$C_{15}H_{17}N_3O$	70,56	6,71	16,46
(VII)	CH_3	H_2	B	34	224–226 benzene — hexane	71,18	7,06	15,46	$C_{16}H_{19}N_3O$	71,35	7,11	15,60
(VIII)	C_6H_5	H_2	B	38	145–147 benzene	75,85	6,51	12,30	$C_{21}H_{21}N_3O$	76,10	6,38	12,67
(IX)	H	A	A	18	214–216 alcohol	79,57	5,73	9,64	$C_{20}H_{16}N_2O$	79,98	5,36	9,33
(X)	H	B	B	22	216–218 $CHCl_3$	71,56	6,81	14,65	$C_{24}H_{26}N_4O$	71,58	6,78	14,50
(XI)	C_6H_5	B	B	16	187–190 benzene — hexane	77,51	6,44	12,49	$C_{30}H_{30}N_4O$	77,90	6,53	12,11

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* Hydrochloride.

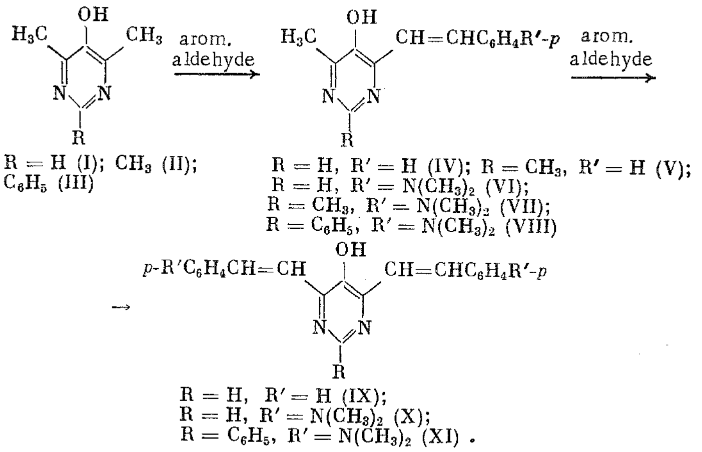
† Calculated on the basis of unreacted starting compound. A = $=CH—C_6H_5$; B = 

These facts were the basis for studying the reactivity of the CH_3 groups of 4,6-dimethyl-5-hydroxypyrimidine (I) and its derivatives (II), (III), in condensation with benzaldehyde and p-dimethylaminobenzaldehyde (scheme).

We found that when the reaction was carried out at 100°C in the presence of HCl, mixtures of mono- and distyrylpyrimidines were formed, which were not formed in basic conditions, probably due to the impossibility of protonation of a ring nitrogen under basic conditions. This protonation is necessary to increase the reactivity of the methyl group. All of the reactions were equilibria, and could not be carried to the end, even by increasing reaction times or temperatures. Physical constants and yields for the compounds synthesized are given in Table 1.

The introduction of a methyl, or especially of a phenyl, group into the 2-position of (I) essentially decreases the extent of condensation. For example, compound (III) did not react with benzaldehyde, probably due to the strong positive mesomeric effect of the C_6H_5 group, which decreases the reactivity of the CH_3 group.

Scheme



R = H (I); CH_3 (II); C_6H_5 (III)

R = H, R′ = H (IV); R = CH_3, R′ = H (V);
R = H, R′ = $N(CH_3)_2$ (VI);
R = CH_3, R′ = $N(CH_3)_2$ (VII);
R = C_6H_5, R′ = $N(CH_3)_2$ (VIII)

R = H, R′ = H (IX);
R = H, R′ = $N(CH_3)_2$ (X);
R = C_6H_5, R′ = $N(CH_3)_2$ (XI) .

Structures of the synthesized styryl-5-hydroxypyrimidines were determined by NMR spectra. All compounds had the trans configuration (J = 18 Hz). The compounds were colored from lemon-yellow to dark violet and possessed indicator properties. When dissolved in organic solvents they gave orange-red or yellow-green fluorescence (Fig. 1).

Comparison of the data for the reactivity of the CH_3 group in 2-hydroxy-4-methyl- and 4,6-dihydroxypyrimidines [3] with our results shows the increased reactivity of methyl-substituted 5-hydroxypyrimidines.

The lower reactivity of 2- and 4-hydroxypyrimidines in condensations with aldehydes is probably caused by their predominant existence as carbonyl tautomers, in which the methyl protons possess a lower reactivity.

EXPERIMENTAL

NMR spectra were taken on an HA-100 instrument at 29° on 8-10% solutions in CD_3OD and $CDCl_3$, with hexamethyldisilane as internal standard. The accuracy of determination was $\delta \pm 0.02$.

Synthesis of 4(6)-styryl-5-hydroxypyrimidines. A mixture of 0.005 mole of (I), (II) or (III) and 0.01 mole of aldehyde was heated for 2 h on a boiling water bath with 10-20 ml of 5% HCl. The hot reaction mixture was evacuated to remove unreacted aldehyde (C_6H_5CHO). The mixture was then cooled and neutralized with Na_2CO_3. A solid precipitated. The solid was dried, dissolved by heating in a suitable solvent, filtered from inorganic salts, separated on a 40×100 μm silica gel (from Czechoslovakia) column, and eluted with acetone, ethyl acetate, and ether. Experimental data are given in Table 1.

CONCLUSIONS

1. 4,6-Dimethyl-5-hydroxypyrimidines with methyl or phenyl groups in the 2-position were condensed with aromatic aldehydes to give styrylpyrimidines.

2. A hydroxyl group in the 5-position of the pyrimidine ring did not prevent the condensation, in contrast to hydroxyl groups in the 2- or 4-position.

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PHOTOCHEMICAL TRANSFORMATIONS OF POLYFLUORO-SUBSTITUTED STILBENES

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We have already discovered a new type of photocyclization of fluoro-substituted N-alkyldiarylamines into carbazoles [1] and of anils of polyfluoroaromatic ketones into phenanthridines [2] with splitting of the aromatically bound fluorine. In the present work, we studied the possible realization of a similar photoreaction for 2,3,4,5,6-pentafluorostilbene. We know that during UV irradiation of their dilute solutions in organic solvents, stilbenes may undergo the photocyclization of an oxidative (with splitting of two H atoms) and nonoxidative type (with splitting of HX, where X = OMe, I) into derivatives of phenanthrene [3].

trans-2,3,4,5,6-Pentafluorostilbene (I) was synthesized by the Wittig reaction from pentafluorobenzaldehyde and benzylidenetriphenylphosphorane. An attempt to obtain (I) according to [4] by the reaction of pentafluorobenzaldehyde with $PhCH_2MgCl$ was unsuccessful.

It is known that the synthesis of the perfluorinated analog of (I) by the Wittig reaction leads to the formation of a mixture of cis- and trans-isomers [5]. For the stilbene (I) which we obtained, there are three signals in the ^{19}F NMR spectrum with an intensities ratio of 2:1:2, characteristic of the C_6F_5 group. The data of elemental analysis and the value of the molecular weight, determined mass spectrometrically, correspond to the empirical formula $C_{14}H_7F_5$. In the PMR spectrum, besides the signal of aromatic protons, an AB system with $J = 18$ Hz is also observed, corresponding to the trans-orientation of the vicinal olefinic protons [6]. The melt-

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