PMR spectrum: 1.83 (2H, quintet, 6-CH$_2$), 2.27 (2H, t, 5-CH$_2$), 3.29 (2H, q, 7-CH$_2$), 3.7 (3H, s, OCH$_3$), 6.73 and 6.80 (4H, d, aromatic CH=), 8.34 (1H, t, 1-NH), and 8.58 ppm (1H, s, NH).

2-Oxo-3-phenylamino-4-cyano-2H-1,5,6,7-tetrahydroazepine (VIa). This compound was similarly obtained (Table 1). PMR spectrum: 1.85 (2H, quintet, 6-CH$_2$), 2.33 (2H, t, 5-CH$_2$), 3.61 (2H, q, 7-CH$_2$), 6.87-7.18 (m, aromatic CH=), and 8.45 ppm (1H, t, 1-NH).

2-Oxo-3-(p-chlorophenyl)amino-4-cyano-2H-1,5,6,7-tetrahydroazepine (VIc). This compound was similarly obtained (Table 1). PMR spectrum: 1.85 (2H, quintet, 6-CH$_2$), 2.31 (2H, t, 5-CH$_2$), 3.30 (2H, q, 7-CH$_2$), 6.83 and 7.29 (4H, d, aromatic CH=), and 8.48 ppm (1H, t, 1-NH).

3-Amino-8-oxo-8H-4,5,6,7-tetrahydropyrazolo[5,4-c]azepine (VII). A mixture of 1.5 g (10 mmole) of hydroxy nitrile IV, 0.55 g (11 mmole) of hydrazine hydrate, and 20 ml of absolute alcohol was refluxed for 1.5 h, after which it was worked up to give VII (Table 1). PMR spectrum: 1.96 (2H, m, 5-CH$_2$), 2.61 (2H, t, 4-CH$_2$), 3.35 (2H, q, 6-CH$_2$), and 7.91 ppm (1H, t, NH).

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REACTION OF METHYLPYRIMIDINES WITH TRICHLORO- AND TRIFLUOROACETYL CHLORIDES

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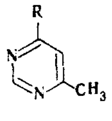
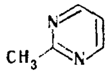
UDC 547.853.4'464.2

The corresponding trichloro- and trifluoroacetonylpyrimidines were obtained by reaction of 2- and 4-methylpyrimidines with trichloro- and trifluoroacetyl chlorides.

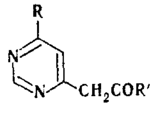
It is known [1, 2] that phenacylpyrimidines are formed in the reaction of 4,6-dimethylpyrimidine with aromatic acid chlorides in the presence of triethylamine. In the present research we studied the reaction of methylpyrimidines with trichloro- and trifluoroacetyl chlorides; this reaction leads to α-halo ketones of the pyrimidine series.



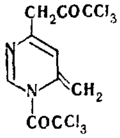
I-III



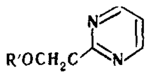
IV



V-IX



X



XI, XII

I R=CH$_3$; II R=OCH$_3$; III R=H; V R=CH$_3$, R'=CCl$_3$, VI R=OCH$_3$, R'=CCl$_3$, VII R=H, R'=CCl$_3$, VIII R=CH$_3$, R'=CF$_3$, IX R=H, R'=CF$_3$; XI R'=CCl$_3$; XII R'=CF$_3$

The reaction of methylpyrimidines I-IV with the acid chlorides in the presence of triethylamine proceeds vigorously as the mixtures are cooled. The amino alkenone, which is readily formed by the action of tertiary amines on the perhalo acid chlorides, was therefore obtained in only 1% yield in our case.

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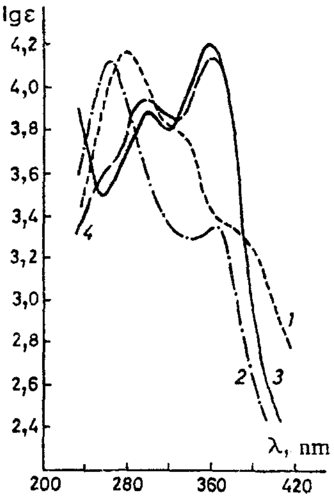

Fig. 1. UV spectra (c 10^{-2} M): 1) XI; 2) XII; 3) VI; 4) VIII.

TABLE 1. Parameters of the PMR and UV Spectra of Trichloro- and Trifluoroacetonylpyrimidines

Compound	Solvent	Chemical shifts, ppm					Note	Tautomers, %		$\frac{\varepsilon^{360*}}{\varepsilon^{360}}$
		=CH	CH_2	H^2	H^4	H^5		=CH	CH_2	
V	CCl_4	6,17 (s)	2,40 (s)	8,96 (s)	—	6,91 (s)	CH_3 2,70 (s)	41	59	2.8
VI	CCl_4	6,30 (s)	2,36 (s)	9.10 (s)	—	6.55 (s)	OCH_3 4.34 (s)	67	33	1,9
	$CDCl_3$	6,41 (s)	2,52 (s)	8.91 (s)	—	6,63 (s)	OCH_3 4,39 (s)	75	25	
VII	CCl_4	5,90 (s)	—	8,61 (s)	7,97 (d)	6,69 (d)	$J=6$ Hz	100	0	1,8
VIII	CCl_4	5.94 (s)	2,35 (s)	8,97 (s)	—	7,00 (s)	CH_3 2,75 (s)	36	64	1.6
XI	CCl_4	6,81 (s)	2.37 (s)	—	8.96 (d)	7.36 (t)	$J=5$ Hz	42	58	0.4
	$CDCl_3$	6.91 (s)	2,54 (s)	—	9.00 (d)	7,45 (t)	$J=5$ Hz	62	38	
XII	CCl_4	6,47 (s)	2,35 (s)	—	8,93 (d)	7,39 (t)	$J=5$ Hz	79	21	0,2

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*This is the ratio of the extinction coefficients at the maximum of the corresponding UV absorption bands; the solvent was CH_2Cl_2.

4-Methyl- and 4-methoxy-6-trichloroacetonylpyrimidines (V and VI) and 4- and 2-trichloroacetonylpyrimidines (VII and XI) were obtained from methylpyrimidines I-IV and trichloroacetyl chloride.

4-Methyl-6-trifluoroacetonylpyrimidine (VIII) and 4- and 2-trifluoroacetonylpyrimidines (IX and XII) were obtained by reaction of pyrimidines I, III, and IV with trifluoroacetyl chloride. In addition to V, N-trichloroacetyl-4-methylene-6-trichloroacetonylpyrimidine (X) was isolated when a large excess of the acid chloride was used in the reaction with 4,6-dimethylpyrimidine I. The N—CO bond in the trichloroacyl group of X is weak and is hydrolyzed even when X is heated in nonabsolute organic solvents. The ease of the X → V transformation confirms that the acylation of pyrimidine I takes place at the methyl group and the ring nitrogen atom.

We were unable to isolate N-acyl derivatives in any of the remaining cases.

The IR spectra of V, VI, and VIII-XII contain absorption bands at 1450 (CH_2CO) and 1640 cm^{-1} (C=O).

The PMR spectra of V-VIII, XI, and XII contain characteristic groups of signals at 2.3-2.6, 5.9-6.9, and 6.5-9.1 ppm, which were assigned to the methylene, olefin, and aromatic protons, respectively. The effect of a polar solvent is manifested as a low-field ∿ 0.2 ppm shift of the signals. An intense long-wave band is observed at 360 nm in the UV spectra

TABLE 2. Pyrimidines V-XII

Compound	mp, °C	R_f	Found, %				Empirical formula	Calc., %				Yield, %
			C	H	Cl	N		C	H	Cl	N	
V	147—148[a]	0,87	38,1	2,7	—	10,9	$C_8H_7Cl_3N_2O$	37,9	2,8	—	11,1	34
VI	135—136[a]	0,71	35,5	2,6	39,9	10,3	$C_8H_7Cl_3N_2O_2$	35,6	2,6	39,8	10.4	54
VII	126—128[a]	0,77	35.1	2,1	44,3	11,5	$C_7H_5Cl_3N_2O$	35,1	2,1	44,4	11,7	63
VIII	129—131[a]	0,65	47,1	3,7	—	13,3	$C_8H_7F_3N_2O$	47.1	3.5	—	13,7	20
IX	180—180,5[a]	0,79	44.3	2,9	—	14.8	$C_7H_5F_3N_2O$	44,2	2,6	—	14,7	16
X	139—141[b]	0.95	30,3	1,3	53.7	7,4	$C_{10}H_6Cl_6N_2O_2$	30,1	1,3	53,3	7,0	18
XI	98—99[a]	0,91	35.1	1,9	43.9	11,3	$C_7H_5Cl_3N_2O$	35,1	2,1	44,4	11.7	11
XII	116—117[a]	0,85	43,9	2,7	c	—	$C_7H_5F_3N_2O$	44,2	2,6	—	—	7

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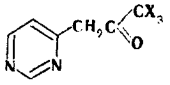
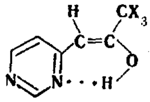
[a] From petroleum ether. [b] By reprecipitation from methanol by the addition of water. [c] Found: F 29.7%. Calculated: F 29.9%.

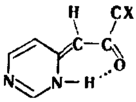
of VI and VIII (Fig. 1) (the character of the curves of V and VII is similar). The data obtained make it possible to assume that an equilibrium involving three tautomeric forms is realized in solutions of trichloro- and trifluoroacetonylpyrimidines:



A

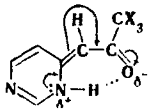


B



C

Because of rapid exchange of the chelated proton (according to the IR spectra, a free NH group does not develop up to concentrations of 10^{-4} M and temperatures of 70°C in CCl_4), the signal of the methylidyne proton in the PMR spectra is averaged for the pyrimidylidene (C) and enol (B) forms. The UV spectra of the A and B forms contain close absorption that coincides with the absorption of substituted pyrimidines (below 300 nm); the absorption band in the long-wave region was assigned to tautomer C. Long-wave absorption has also been noted for some other tautomeric systems [4, 5]; however, its nature was not established. It is possibly a band of intramolecular charge transfer from the unshared electron pair of the ring nitrogen atom to the oxygen atom of the carbonyl group in agreement with the structure



The ratios of the molar extinction coefficients of the absorption bands of tautomers A and B and of tautomer C are presented in Table 1. The combined use of these data and the PMR data make it possible to draw qualitative conclusions regarding the ratio of the three forms in the solutions. Thus primarily the A and C forms are realized in the case of VI in $CDCl_3$, whereas the C ⇄ B equilibrium with predominance of the C form exists in the case of VII in CCl_4 and CH_2Cl_2.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra were recorded with a Specord UV-vis spectrophotometer. The PMR spectra were obtained with a BS-487B spectrometer (80 MHz) at room temperature with hexamethyldisiloxane as the external standard. The individuality of the compounds obtained was monitored by thin-layer chromatography (TLC) on activity II Al_2O_3 in a chloroform—methanol system (5:2) with development in UV light.

Reaction of Methylpyrimidines I-IV with Trichloro- and Trifluoroacetyl Chlorides. A solution of 30 mmole of trichloroacetyl chloride in 10 ml of benzene was added gradually with stirring at 0°C to a solution of 10 mmole of the methylpyrimidine in 30 mmole of triethylamine in 10 ml of benzene (or 30 mmole of trifluoroacetyl chloride was passed into the solution), and the mixture was stirred at room temperature for 1 h. The precipitated triethylamine hydrochloride was removed by filtration, and the filtrate was evaporated in vacuo. The resinous precipitate was extracted with several portions of boiling petroleum ether, the extract was cooled, and the precipitated V, VI, VIII, IX, XI and XII were removed by filtration (Table 2).

In the case of the preparation of V the petroleum ether was removed by vacuum evaporation to dryness, and the residue was dissolved in methanol. The addition of water precipitated 0.02 g (1%) of 1-diethylamino-4,4,4-trichloro-1-buten-3-one with mp 55-56°C (55-56°C [3]).

4-Trichloroacetonylpyrimidine (VII). This compound was obtained by the method presented above. After separation of the triethylamine hydrochloride, the filtrate was evaporated, and the residue was dissolved in methanol and precipitated by the addition of water to give 1.4 g of VII.

N-Trichloroacetyl-4-methylene-6-trichloroacetonylpyrimidine (X). This compound was similarly obtained, but 60 mmole of trichloroacetyl chloride was used in the reaction. Workup of the reaction mixture gave 0.9 g of a mixture of V and X. Fractional reprecipitation from methanol by the addition of water gave 0.1 g of V and 0.7 g of X (Table 2). A 0.1 g sample of X was heated in petroleum ether for 3 h, after which the solution was evaporated in vacuum to give 0.07 g of V with mp 147-148°C.

The synthesized trichloro- and trifluoroacetonylpyrimidines were light-yellow crystalline substances.

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PYRIMIDINES.

LXIV.* STRUCTURE AND PROPERTIES OF 1,3-DIARYLDIHYDROBENZO[f]QUINAZOLINES

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It is shown that the 1,3-diaryldihydrobenzo[f]quinazolines that are formed in the condensation of β-naphthylamine, an aromatic aldehyde, and ammonia are 1,2-dihydro isomers. They readily form salts due to the developing stabilization of the molecule by resonance of the amidinium type. Thus 2,4-dialkylbenzo[f]quinazolinium iodides rather than monoalkyl derivatives were obtained in the case of alkylation with alkyl halides as a result of refluxing the reaction mixtures. The isomeric monoalkylbenzoquinazolinium iodides, the structure of which was proved by the formation of the known benzoquinazolines after treatment with alkali, were also obtained.

We have previously reported [2] that the reaction of β-naphthylamine, an aromatic aldehyde, and ammonia leads to the formation of dihydro derivatives of 1,3-diarylbenzo[f]quinazolines (I). The formation of dihydro derivatives rather than aromatic compounds is probably due to the peculiarities of the structure of the former: first, the presence of a bulky substituent in the 1 position of the benzoquinazoline hinders aromatization of the molecule under the reaction conditions [2], and, second, the existence of a saturated node

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*See [1] for communication LXIII.

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