CHEMICAL PROPERTIES OF YLIDENE DERIVATIVES OF AZINES.

1. STRUCTURE OF THE PRODUCTS OF PROTONATION OF DIHYDRO-2-PYRIMIDYLIDENE- AND DIHYDRO-4-PYRIMIDYLIDENECYANOACETIC ESTERS

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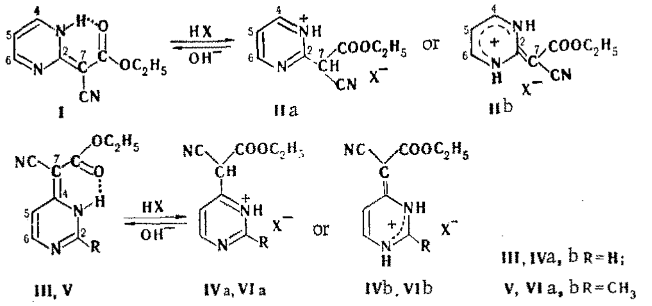
The structure of the products of protonation of dihydro-2-pyrimidylidene- and dihydro-4-pyrimidylidenecyanoacetic esters was investigated by means of IR, UV, and ^{1}H and ^{13}C NMR spectroscopy. It is shown that, in contrast to the corresponding α-derivative of pyridine, the investigated compounds have an ylidene structure in solutions of strong acids and in the form of perchlorates; the protons are attached to the heterocyclic nitrogen atoms.

The tautomeric transformations of pyrimidylmethane derivatives that contain acceptor substituents in the methyl group, including the relatively easily obtained pyrimidylcyanoacetic esters, have been previously studied [1-5]. It was shown that the latter in solid form and in most organic solvents exist in the form of dihydropyrimidylidenecyanoacetic esters (ylidene derivatives), which substantially modifies the properties of the ring framework of the molecule. The structures of their protonation products are examined in the present paper in order to study the chemical properties and possibilities of the subsequent use of the ylidene derivatives of azines for synthetic purposes.

The products of protonation of both the dihydro-2-pyrimidylidene- and dihydro-4-pyrimidylidenecyanoacetic esters (I, III, and V) proved to be quite stable compounds in the form of perchlorates (the analytical and spectral characteristics are presented in Tables 1 and 2), and we propose to continue our study of their reactivities.

Starting esters I and V were synthesized by heteroarylation of the sodium salt of cyanoacetic ester with the corresponding chloropyrimidines. Because of the instability of 4-chloropyrimidine, unsubstituted 3,4-dihydro-4-pyrimidylidenecyanoacetic ester (III) was obtained by catalytic dechlorination of 6-chloro-3,4-dihydro-4-pyrimidylidenecyanoacetic ester (VII).



When esters I, III, and V are dissolved in acidic media, one might expect the formation of products of protonation at both the carbon atom of the side chain (structures IIa, IVa, and VIa) and the ring nitrogen atom attached to a double bond (structures IIb, IVb, and VIb); the latter is more likely, since it is known from the literature that the protonation of similarly constructed oxodihydropyrimidines takes place at the heterocyclic nitrogen atom [6].

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TABLE 1. Analytical Characteristics of the Compounds Obtained

Compound	mp, °C	Found, %				Empirical formula	Calculated, %				Yield, %
		C	H	Cl	N		C	H	Cl	N	
I	190—193^a	56,1	4,70	—	22,2	$C_9H_9N_3O_2$	56,5	4,75	—	22,0	30—50
IIb^b	183—185^c	36,9	3,45	12,2	14,4	$C_9H_9N_3O_2 \cdot HClO_4$	37,1	3,46	12,2	14,4	79
III	190—195^a	55,8	4,80	—	21,7	$C_9H_9N_3O_2$	56,5	4,75	—	22,0	16
IVb^b	188—192^c	36,9	3,60	12,2	14,6	$C_9H_9N_3O_2 \cdot HClO_4$	37,1	3,46	12,2	14,4	75
VIb^b	169—172^c	39,3	3,96	12,1	13,4	$C_{10}H_{11}N_3O_2 \cdot HClO_4$	39,3	3,96	11,6	13,8	67
VII	235—237^a	48,2	3,56	15,7	18,6	$C_9H_8ClN_3O_2$	47,9	3,67	15,7	18,6	50—70
IX^b	122—124,5^d	41,4	3,79	12,5	9,51	$C_{10}H_{10}N_2O_2 \cdot HClO_4$	41,3	3,81	12,2	9,64	92

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[a] From ethanol. [b] $X = ClO_4$. [c] From acetonitrile. [d] From acetic acid.

Solutions of the ylidene derivatives (I, III, and V) of pyrimidine in trifluoroacetic and sulfuric acids are yellow-orange, and the long-wave absorption maxima are retained in the UV spectra of these solutions. The same pattern with retention of the absorption maxima is also observed in the UV spectra of solutions of salts II, IV, and VI ($X = ClO_4$) in trifluoroacetic acid and acetic anhydride (see Table 2).

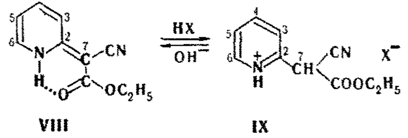
Absorption bands of a conjugated nitrile group at 2225-2240 cm^{-1} are observed in the IR spectra of these salts (in mineral oil) and solutions of I, III, and V in trifluoroacetic and sulfuric acids.

A shift of the signals of the heteroaromatic protons to weak field as compared with the spectrum of I in neutral solvents can be noted in the PMR spectra of solutions of I in acids and of salt II ($X = ClO_4$) in acetonitrile (see Table 2). The 5-H signal shows up in the form of a triplet, and the width and multiplicity of the 4- and 6-H signals depend substantially on the solvent and temperature; this is evidently associated with the different degree of protonation of I and intermolecular exchange between the protonated and unprotonated forms.

We observed a shift of the 5-H signals to weak field and of the 6-H signals to strong field in the PMR spectra of solutions of III and V in CF_3COOH and H_2SO_4, as well as in the spectra of salts IV and VI ($X = ClO_4$) in acetonitrile, as compared with the spectra of III and V in $CDCl_3$. It is important to note that signals of methylidyne protons are absent in the PMR spectra for both 2- and 4-ylidene derivatives I, III, and V in solutions of acids, as well as for solutions of their salts II, IV, and VI. Signals of an NH group appear only in the PMR spectra of solutions of salts II, IV, and VI in acetonitrile, in which the intermolecular exchange mentioned above is retarded; the form of the 4- and 6-H (for II) and 2- and 6-H (for IV and VI) signals is complicated in the same way as in the PMR spectra of 2- and 4-oxodihydropyrimidines in solutions of acids at low temperatures [6].

Upon the whole, the data from the IR, UV, and PMR spectra of solutions of I, III, and V in acids and of their salts are in good agreement with the formation of N-protonation products IIb, IVb, and VIb.

However, the examined spectral data also do not repudiate partial protonation of I, III, and V with the formation of aromatic structures IIa, IVa, and VIa, which exist in rapid exchange with the unprotonated form. The spectral data for 1,2-dihydro-2-pyridylidenecyanoacetic ester (VIII) in solution in CF_3COOH constitute an example of this case. We used this compound as a model ylidene compound of the pyridine series that contains a cyanoacetic ester residue (see [7] for evidence for ylidene structure VIII). For it, on the basis of the literature data [8, 9] for solutions in strong acids, one might have expected the formation of only a protonation product with aromatic structure IX; this is confirmed unambiguously by disappearance of the long-wave absorption maximum in the UV spectra if protonation of VIII takes place sufficiently completely (see the UV spectrum of VIII in H_2SO_4 solution, Table 2). We also obtained solid salt IX ($X = ClO_4$), the analytical and spectral characteristics of which are presented in Tables 1 and 2.



VIII IX

Only a decrease in the intensity of the long-wave absorption maximum is observed in the UV spectrum of VIII in solution in CF_3COOH, and the absorption band of a conjugated nitrile group is retained in the IR spectrum of VIII in the same solvent; only partial protonation of VIII consequently occurs in a solution of this acid. A shift of the signals of the heteroaromatic protons to weak field occurs in the PMR spectrum of VIII in trifluoro-

TABLE 2. UV and PMR Spectra of I-VI, VIII, and IX

Compound	Solvent	UV spectrum, λ_{max}, nm (log ε)	Solvent	PMR spectrum, ppm				
				CH_2CH_3	OCH_2	N—H	heteroaromatic protons	other protons
I	C_2H_5OH	300 (4,45), 380 (3,53)	$CDCl_3$[a]	1,40 t	4,25 q	13,7 br s	6,60 (m, 5-H); 7,85 (m, 4-H); 8,75 (m, 6-H)	
	CF_3COOH	293 (4,62), 400 (3,06)	CF_3COOH	1,37 t	4,41 q	—	7,18 (t, 5-H); 8,85 (d, 4-H and 6-H)	
	H_2SO_4	296 (4,45), 390 (3,06)	$CF_3COOH—HSO_3F$	1,38 t	4,43 q	—	7,32 (t, 5-H); 8,93 (m, 4-H and 6-H)	
IIb[b]	$(CH_3CO)_2O$	299 (4,31), 400 (2,98)	CH_3CN	1,45 t	4,25 q	10,7 br s	7,05 (t, 5-H); 8,70 (m, 4-H and 6-H)	
III	C_2H_5OH	303 (4,15), 342 (4,10)	$CDCl_3$	1,31 t	4,24 q	13,7 br s	7,07 (d, 5-H); 8,01 (d, 6-H); 8,24 (s, 2-H)	
	CF_3COOH	313 (4,32)	CF_3COOH	1,37 t	4,41 q	—	7,31 (d, 5-H); 7,83 (d, 6-H); 9,15 (s, 2-H)	
	H_2SO_4	318 (4,27)	H_2SO_4	1,50 t	4,55 q	—	7,40 (d, 5-H); 7,95 (m, 6-H); 9,03 (m, 2-H)	
IVb[b]	CF_3COOH	312 (4,32)	CH_3CN	1,30 t	4,33 q	9,55 br s	7,17 (d, 5-H); 7,73 (m, 6-H); 8,93 (m, 2-H)	
V	C_2H_5OH	300 (4,04), 347 (4,23)	$CDCl_3$[a]	1,33 t	4,25 q	13,6 br s	6,93 (m, 5-H); 7,96 (d, 6-H)	2,54 (s, 2-CH_3)
	CF_3COOH	310 (4,35)	CF_3COOH	1,38 t	4,40 q	—	7,18 (d, 5-H); 7,70 (d, 6-H)	2,91 (s, 2-CH_3)
	H_2SO_4	315 (3,81)	H_2SO_4	1,50 t	4,53 q	13,6 br s	7,25 (d, 5-H); 7,80 (m, 6-H)	3,00 (s, 2-CH_3)
VIb[b]	$(CH_3CO)_2O$	313 (4,35)	CH_3CN	1,30 t	4,30 q	10,5 br s	7,05 (d, 5-H); 7,60 (m, 6-H)	3,07 (s, 2-CH_3)
	CF_3COOH	312 (4,38)						
VIII	C_2H_5OH	223 (4,08), 295 (4,29), 373 (4,00)	$CDCl_3$[a]	1,30 t	4,22 q	14,0 br s	6,76 (m, 5-H); 7,32 (m, 3-H); 7,67 (m, 4-H); 7,92 (m, 6-H)	
	CF_3COOH	260 (3,86), 284 (3,70), 360 (3,53)	CF_3COOH	1,30 t	4,37 q	—	7,55—8,62 m	
	H_2SO_4	260 (3,79)	H_2SO_4	1,42 t	4,60 q	13,40 br s	8,15—9,15 m	5,80; 5,90 (s, 7-H)
IX[b]	$(CH_3CO)_2O$	—	CH_3CN	1,25 t	4,30 q		8,00—8,90 m	5,70 br s, 7-H)
			$(CH_3CO)_2O$	1,00 t	4,10 q	13,79 br s	7,99—8,98 m	5,79 br s, 7-H)

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[a] See [3, 7] for the literature data. [b] $X = ClO_4$.

TABLE 3. ^{13}C NMR Spectra of I-VI, VIII, and IX

Compound	Solvent	Chemical shifts, ppm, relative to tetramethylsilane ($J_{^{13}C-H}$, Hz)^a									
		C_2	C_4	C_5	C_6	C_7	CN	CO	OCH_2	CH_3	other C atoms
I	CH_2Cl_2—d_6-DMSO	161,2 s	144,3 d	108,9 d	163,8 d	65,6 s	118,2 s	169,3s	60,0 t	14,2 q	—
I	CF_3COOH	154,5 s	156,8 d	109,7 d	158,9 d	66,8 s	113,8 s	168,7s	64,7 t	13,0 q	—
I	CF_3COOH—HSO_3F	153,6	158,4	110,3	158,4	66,6	—	168,3	65,3	13,1	—
IIb^b	$(CH_3CO)_2O$	153,3 s	158,8 d	109,8 d	158,8d	66,7 s	114,2 s	168^c	63,3 t	14,5 q	—
III	CH_2Cl_2	146,8	156,2	114,9	153,0	66,7	116,7	169,2	61,3	14,4	—
III^b	CF_3COOH	150,1 d	153,4 s	116,5 d	137,1 d	78,5 s	—	167,7s	65,0 t	12,8 q	—
IVb^b	CH_3CN	151,1	153,2	116,7	137,6	78,8	115,2	167,2	63,8	14,5	—
V	$CDCl_3$	156,8	156,4	111,4	153,0	65,7	116,6	169,2	60,8	14,2	22,4 (2-CH_3)
V	CF_3COOH	162,6 s	154,8 s	114,1d	137,6 d	77,8 s	113,2	168,3	65,0 t	13,2 q	19,1 q (2-CH_3)
VIb^b	CH_3CN	162,2	154,3	114,2	138,1	77,8	115,3	168,0	63,9	14,5	20,3 (2-CH_3)
VIb^b	$(CH_3CO)_2O$	162,5 s	154,6 s	113,6 d	138,6 d	77,4 s	115,1s	168^c	63,7 t	14,5 q	20,1 (2-CH_3)
VIII	CH_2Cl_2	155,4 s	139,9d (166)	112,6 d^d (170)	134,6 d (182)	62,0 s	119,1s	170,1s	60,0 t (145)	14,4 q (126)	120,0d (C_3)d (169)
VIII	CF_3COOH	148,4	145,5	122,0^d	139,5	48,8	113,3	166,8	64,4	12,5	124,1 (C_3)^d
VIII	H_2SO_4	143,1s	151,0 d (171)	130,4 d^d (180)	145,0 d (192)	53,3 d (133)	165,7s	173,5s	69,4 t (152)	14,3 q (127)	131,5d (C_3)^d (172)
IX^b	$(CH_3CO)_2O$	144,8 s	150,0d (175)	129,0 d (182)	144,5 d (195)	42,5 d (140,4)	113,5 s	162,6 s	66,0 t (152)	14,2 q (129)	129,0d (C_3)^d (182)

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[a] The numbering of the carbon atoms is presented in the corresponding formulas. [b] $X = ClO_4$. [c] The signal coincides with the signal of the CO group of the solvent. [d] The possibility that the assignment of the C_3 and C_5 signals may be just the opposite is not excluded.

acetic acid, and signals of a methylidyne proton of the side chain and the NH group are not observed. It is apparent that the spectral data obtained for VIII in solution in CF_3COOH are very similar to the data examined above in the case of protonation of ylidene derivatives I, III, and V of pyrimidine.

To obtain more rigorous proof for the structures of the protonated ylidene derivatives I, III, and V of pyrimidine we used ^{13}C NMR spectroscopic data for these compounds and their salts, as well as model α-pyridyl derivative VIII and its salt IX in various media. The chemical shifts of the carbon atoms in the ^{13}C NMR spectra of I-VI, VIII, and IX are presented in Table 3. All of the signals of the carbon atoms in the spectra presented were assigned on the basis of the character of the splitting, the intensities of the signals, and the chemical shifts and spin-spin coupling constants ($J_{^{13}C-H}$). For the assignment of the signals of the carbon atoms we also used the calculated data obtained for unsubstituted dihydro-2-pyrimidylidene- and dihydro-4-pyrimidylidenecyanoacetic acids by the CNDO/2 method.* The total ($\sigma + \pi$) charges on the carbon atoms of these acids and their cations of the IIb, IVb, and VIb type (the numbers in parentheses) are presented in Fig. 1. It is apparent from the calculated data that dihydropyrimidylidenecyanoacetic esters, like enamino ketones, are polar compounds with clearly expressed alteration of the charges in the neutral molecule and cation (cf. [10]).

In an examination of the signals of the heteroaromatic C_2-C_6 atoms in the ^{13}C NMR spectra of I, III, and V in neutral solvents we assigned the signals at strongest field to the C_5 atom starting from the calculated values of the charges on these atoms. In the spectrum of I in CH_2Cl_2-DMSO, in addition to the methods enumerated above, we used selective double resonance for the assignment of the signals of the C_4 and C_6 atoms. A comparison of the spectra of III and V in neutral solvents made it possible to assign the C_2, C_4, and C_6 signals in these spectra (see Table 3).

For α-pyridyl derivative VIII and its salt IX the assignment of the C_3-C_6 signals was made on the basis of the fact that in the spectra of pyridine derivatives the $J_{^{13}C-H}$ value changes in the order $J_{^{13}C_\alpha-H} > J_{^{13}C_\beta-H} > J_{^{13}C_\gamma-H}$ [11].

The analogy between the investigated ylidene derivatives of azines and enamino ketones is further displayed in the fact that the chemical shift of the sp^2-hybridized C_7 atom in the ^{13}C spectra of I, III, V, and VIII in solution in methylene chloride and chloroform has an unusual strong-field value (62-66 ppm) (as compared with 68-70 ppm in the spectra of enamino ketones [12]). The results of the calculations make it possible to explain the reason for this chemical shift of the C_7 atom, which is associated with the negative charge on this atom because of conjugation with the NH group of the heteroring.

On passing from neutral solvents to solutions of I, III, and V in acids and to salts II, IV, and VI, in the ^{13}C NMR spectra one may note that in the case of 2-ylidene derivative I of pyrimidine the signals of the C_4 and C_6 atoms in the spectrum of its salt II become equivalent. In contrast to the spectrum of salt II, two separate signals for the C_4 and C_6 atoms are observed in the spectrum of a solution of I in trifluoroacetic acid; this is associated with incomplete protonation of I in CF_3COOH. The degree of protonation estimated on the basis of differences in the chemical shifts of solutions of I in CH_2Cl_2-DMSO and in CF_3COOH as compared with the spectrum of salt II is $\sim$85%. When the acidity of the medium ($CF_3COOH-HSO_3F$) is increased, the degree of protonation increases, and the spectrum of a solution of I in this medium virtually coincides with the spectrum of salt II. In the case of 4-ylidene derivatives III and V of pyrimidine the spectra of solutions in CF_3COOH coincide with the spectra of salts IV and VI; this is evidently associated with the greater basicity of the 4-ylidene derivatives as compared with the 2-ylidene derivatives.

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* The authors thank V. V. Lapachev for making the calculations.

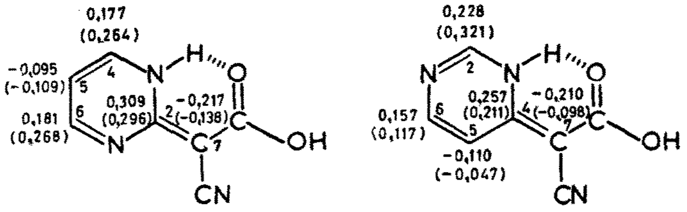

Fig. 1. Total ($\sigma + \pi$) charges on the carbon atoms of dihydro-2-pyrimidylidene- and dihydro-4-pyrimidylidenecyanoacetic acids and their cations of the IIb and IVb type (the charges for the cations are presented in parentheses).

It is apparent from the chemical shifts in the spectrum of a solution of VIII in CF_3COOH that the degree of protonation of the pyridine derivative (~50%) is substantially lower as compared with the corresponding pyrimidine derivatives I, III, and V. The chemical shifts for the carbon atoms of the side chain for solutions of VIII in sulfuric acid differ from those for salt IX (particularly for the CN group). This provides a basis for the assumption that additional protonation in the side chain occurs in this medium. In addition to the principal signals in the ^{13}C NMR spectrum, lower-intensity signals, the chemical shifts of which virtually coincide with the signals of salt IX, are also observed. In the PMR spectrum of this compound in H_2SO_4 we also observed two signals of methylidyne protons at 5.80 and 5.90 ppm (see Table 2).

In the case of α-pyridine derivative VIII the formation of protonation product IX is accompanied by a change in the hybridization of the C_7 atom at which protonation occurs, which gives rise to a shift in the signal of this atom in the ^{13}C NMR spectrum to strong field of ~20 ppm (see Table 3 for the spectrum of IX in acetic anhydride). It is important to note that this signal in the monoresonance spectrum of a solution of VIII in methylene chloride is a singlet, whereas it is a doublet with $J_{^{13}C-H} = 140$ Hz, which is characteristic for an sp^3-hybridized carbon atom, in the case of salt IX in acetic anhydride.

Not even a tendency for the conversion of the C_7 atom to the sp^3-hybridized state, which would be manifested as a shift of the signal to strong field, is observed in the formation of salts II, IV, and VI from ylidene derivatives of pyrimidine. On the other hand, a shift of the signal of the C_7 atom to weak field (to ~ 12 ppm) occurs when I, III, and V are dissolved in acids, and this signal remains a singlet in all cases. A similar weak-field shift (~30 ppm) of the signal of the carbon atom attached to the double bond in enamino ketones occurs in the case of protonation at the nitrogen atom [10, 12].

Thus the ^{13}C NMR spectroscopic data confirm the formation of protonation products IIb, IVb, and VIb and make it possible to calculate the degree of protonation in media with different acidities. From the set of all of the presented data it may be concluded that dihydro-2-pyrimidylidene- and dihydro-4-pyrimidylidenecyanoacetic esters I, III, and V, in contrast to the corresponding α-derivative of pyridine, have ylidene structures IIb, IVb, and VIb in solutions in strong acids and in the form of perchlorates.

EXPERIMENTAL

The IR spectra of samples of the compounds in mineral oil were recorded with a UR-20 spectrometer, while the IR spectra of solutions in CF_3COOH and H_2SO_4 were recorded with a Perkin-Elmer spectrometer in CaF_2 cuvettes with a Teflon inlet (the layer thickness was 0.04 mm). The UV spectra of solutions (10^{-4} mole/liter) of the compounds were recorded with a Specord UV-vis spectrophotometer. The PMR spectra of 7-10% solutions of the compounds at 20°C were recorded with a Varian A-56/60 spectrometer. The ^{13}C NMR spectra were recorded under pulse conditions with subsequent Fourier transformation with a Bruker HX-90 spectrometer at room temperature. Solutions with concentrations of 1 mole/liter were used to record the ^{13}C NMR spectra. Because of the low solubility of I in methylene chloride, several drops of DMSO were added; a saturated solution (~0.2 mole/liter) was used for III in CH_2Cl_2, since the addition of DMSO induces conversion of III to another tautomer [3]. The substances were isolated unchanged, judging from the PMR spectra, from solutions of I, III, V, and VIII in strong acids after neutralization.

1,2-Dihydro-2-pyrimidylidenecyanoacetic Ester (I). A 0.58-g (5 mmole) sample of 2-chloropyrimidine [13], 20 ml of dry dioxane, 0.1 g (3 mmole) of 18-crown-6-ether, and 0.36 g (15 mmole) of sodium hydride were mixed, and 1.7 g (15 mmole) of cyanoacetic ester was added dropwise to the stirred suspension in the course of 15 min. When hydrogen evolution was complete, the reaction mixture was heated gradually to 100°C and maintained at this temperature for 8 h. The course of the reaction was followed by means of thin-layer chromatography (TLC) on Silufol UV-254 plates in ethyl acetate–ethanol (10 : 1) from the disappearance of the spot of the starting 2-chloropyrimidine. The mixture was then diluted with ether, and the yellow precipitate of the Na salt of I was separated and stirred for 1 h in a mixture of 100 ml of methylene chloride and 5 ml of 10% HCl. The organic layer was washed with water, dried, and filtered. Removal of the solvent gave 0.55 g of I.

Dihydro-2-pyrimidylideniacyanoacetic Ester Perchlorate (IIb, $X = ClO_4$). A 1.91-g (0.01 mole) sample of I was dissolved at 60°C in a mixture of 15 ml of acetic anhydride and 15 ml of acetic acid, 1 ml (0.05 mole) of 68% $HClO_4$ was added dropwise with stirring at 20°C to the resulting yellow solution, and the mixture was heated at 60°C for 1 h. It was then cooled to 20°C and diluted with dry ether, and the diluted mixture was allowed to stand overnight. The precipitate was removed by filtration, washed with dry ether, and dried to give 2.3 g of IIb ($X = ClO_4$).

6-Chloro-3,4-dihdro-4-pyrimidylidenecyanoacetic Ester (VII). This compound was obtained from 4,6-dichloropyrimidine [14] by the method in [1].

3,4-Dihydro-4-pyrimidylidenecyanoacetic Ester (III). A 1-g (4.5 mmole) sample of VII was hydrogenated in 15 ml of acetic acid at atmospheric pressure in the presence of 0.5 g of 10% Pd/C and 0.4 g (4.9 mmole) of sodium acetate at 70°C. The course of the reaction was followed by means of TLC on Silufol UV-254 plates in chloroform–ethanol (10 : 1) from the disappearance of the spot of starting VII. After 8 h, ~300 ml of hydrogen (the theoretical amount is ~200 ml) had been absorbed, and the catalyst was removed by filtration and washed with hot acetic acid. The mother liquor was evaporated to dryness in vacuo, and the residue was washed with ethanol and recrystallized from ethanol. The yield of III was 0.14 g.

Perchlorate IVb ($X = ClO_4$) was obtained in the same way as IIb ($X = ClO_4$).

2-Methyl-3,4-dihydro-4-pyrimidylidenecyanoacetic Ester (V). This compound was obtained by the method in [15] and had mp 160-162°C (mp 160°C [3]). Perchlorate VIb ($X = ClO_4$) was obtained in the same way as IIb ($X = ClO_4$).

1,2-Dihydro-2-pyridylidenecyanoacetic Ester (VIII). This compound was obtained by the method in [7] and had mp 104-106°C. Perchlorate IX ($X = ClO_4$) was obtained in the same way as IIb ($X = ClO_4$).

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