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CHEMICAL PROPERTIES OF YLIDENE DERIVATIVES OF AZINES.
5.* BROMINATION OF DIHYDROPYRIDYLIDENE- AND DIHYDROPYRIMIDINYLIDENECYANOACETIC ESTERS

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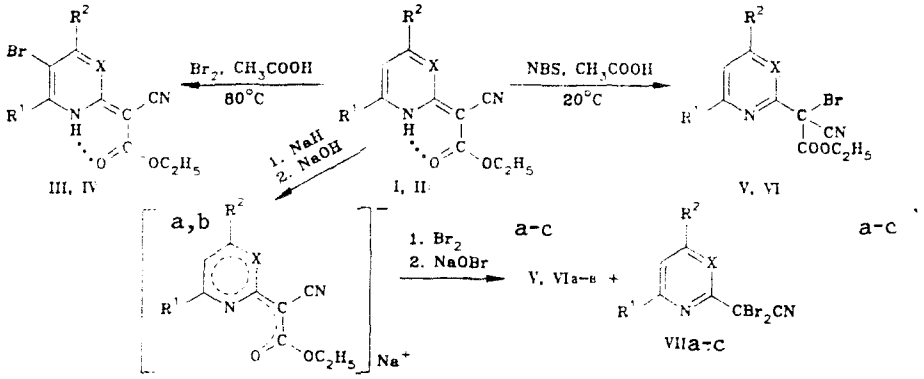
The bromination of dihydro-2-pyridylidene- and dihydro-2-pyrimidinylidenecyanoacetic esters proceeds at the 5-position of the dihydroazine ring under thermodynamically controlled conditions. By using the "kinetically" controlled conditions the products of monobromination in the side chain can be obtained in high yields. By the action of bromine on the sodium salts of substituted dihydro-2-pyrimidinylidenecyanoacetic esters in dimethoxyethane, a mixture of mono- and dibrominated derivatives is formed at the exocyclic carbon atom, while only the corresponding 2-pyrimidinyldibromoacetonitriles are formed by the action of sodium hypobromite in water.

The presence of several nucleophilic reaction centers in the ylidene derivatives of dihydropyridine and -pyrimidine, their possible heteroaromatic tautomers, and the corresponding mesomeric anions may result in their displaying ambient properties in the reactions with electrophilic reagents [2, 3]. We studied the reaction of dihydro-2-pyridylidene- and dihydro-2-pyrimidinylidenecyanoacetic esters (I and IIa-c) with various brominating agents: bromine, N-bromosuccinimide (NBS), and sodium hypobromite.



I, III, V X=CH, $R^1=R^2=H$; II, IV, VI, VII X=N, a $R^1=R^2=H$, b $R^1=H$, $R^2=C_6H_5$, c $R^1=R^2=C_6H_5$

2(1H)-Pyridones, 2(1H)-pyrimidinones, and their N-methyl derivatives react rapidly with bromine in solutions; the bromination in the ring proceeds under mild conditions as a result of a fast reaction of their covalent hydrates with bromine [4, 5].

*For Communication 4, see [1].

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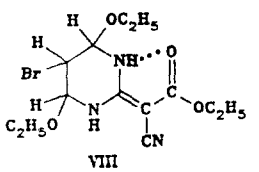
TABLE 1. Characteristics of Compounds III-IX, XIa, b, XIII, XV-XVIII

Compound	Empirical formula	mp, °C (from ethanol)	UV spectrum, λ_{max}, nm (log ε)	IR spectrum, cm^{-1}	
				$\nu_{C=C}$, $\nu_{C=O}$	$\nu_{C\equiv N}$
III	$C_{10}H_9BrN_2O_2$	190...192	207 (4,05), 226 (4,03), 307 (4,30), 395 (3,86)	1520, 1595, 1650	2210
IVb	$C_{15}H_{12}BrN_3O_2$	198...203	202 (4,28), 313 (4,61), 407 (3,43)	1500, 1530, 1580, 1610, 1655	2210
V	$C_{10}H_9BrN_2O_2$	Oil	206 (3,96), 237 (3,58)	1580, 1740, 1780	
VIa	$C_9H_8BrN_3O_2$	Oil	213 (3,93), 242 (3,67)	1555, 1620, 1680, 1770, 1790	
VIb	$C_{15}H_{12}BrN_3O_2$	80...82,5	210 (4,30), 236 (3,98), 273 (4,26)	1530, 1585, 1760, 1790	
VIc	$C_{21}H_{16}BrN_3O_2$	108...111	202 (4,54), 263 (4,44), 300 (4,30)	1525, 1580, 1760, 1780	
VIIa	$C_6H_3Br_2N_3$	Oil	205 (4,32), 241 (4,08)	1575, 1595, 1695	
VIIb	$C_{12}H_7Br_2N_3$	152...155	202 (4,31), 215 (4,11), 234 (4,27)	1550, 1590	
VIIc	$C_{18}H_{11}Br_2N_3$	193...196	200 (4,58), 267 (4,41)	1525, 1580, 1590	
VIII	$C_{13}H_{20}BrN_3O_4$	128...133	205 (4,16), 215 (3,95), 256 (4,36)	1560, 1615, 1665	2205
IX	$C_{11}H_{16}BrN_3O_4$	133,5... 135,5	206 (4,09), 217 (3,97), 256 (4,37), 312 (2,66)	1560, 1625, 1665	2210
XIa	$C_{11}H_{11}BrN_2O_2$	158...159	206 (4,02), 222 (4,06), 306 (4,42), 388 (3,96)	1510, 1590, 1660	2210
XIb	$C_{10}H_{10}BrN_3O_2$	137...139	212 (4,25), 240 (3,72), 307 (4,61), 398 (3,46)	1500, 1530, 1580, 1610, 1655	2210
XIII	$C_{15}H_{13}BrN_2O_4$	115...117	207 (4,25), 242 (4,03), 268 (4,17)	1570, 1710, 1760, 1790	
XV	$C_{15}H_{12}BrN_3O_2$	55...57	215 (4,37), 269 (4,21)	1560, 1585, 1755	
XVI	$C_{13}H_8N_4$	286...288 (dec.)	205 (3,42), 308 (3,70), 413 (4,52)	1580, 1615	2180, 2210
XVII	$C_{13}H_7BrN_4$	210...213	204 (4,32), 305 (4,57), 405 (3,45)	1510, 1590, 1620	2195, 2215
XVIII	$C_{13}H_7BrN_4$	92...94	206 (4,42), 259 (4,39)	1555, 1590	

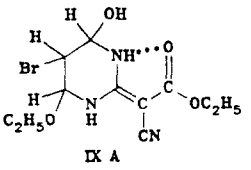
We found that by the action of bromine in acetic acid on dihydroazinylidenecyanoacetic esters I and IIa, b, in solution of which the polar ylidene form (see [6, 7]) predominates, results in the formation of 5-bromo-1,2-dihydro-2-pyridylidene-, 5-bromo-1,2-dihydro-2-pyrimidinylidene- and 5-bromo-4-phenyl-1,2-dihydro-2-pyrimidinylidenecyanoacetic esters (III, IVa, and IVb). According to the PMR spectral data of the reaction mixtures of dihydroazines I and IIa the substituted hexahydropyridines and hexahydropyrimidines are possibly formed at the beginning of the reaction (at 20°C after 1-2 h), (absence of signals of heteroatomatic protons in the 5.5-9.0 ppm region). These compounds, detected by the TLC method (R_f ~ 0.5 in chloroform; detection in UV light) are probably structurally analogous to the addition products of halogens and the solvent to 2(1H)-pyridones, 2(1H)-pyrimidinones and uracils [4, 5, 8, 9]. In the course of 30-40 h at 20°C, they convert into the bromo-substituted dihydroazines III and IVa. The same reaction at 80°C is concluded in 3-4 h.

In the reaction of 4-phenyldihydropyrimidine IIb with bromine in acetic acid (20°C), together with the analogous hexahydropyrimidines, according to the TLC data, 4-phenyl-2-pyrimidinylbromocyanoacetic ester (VIb) is formed — a product of bromination of compound IIb in the side chain. All these compounds convert into 5-bromo-4-phenylhydropyrimidine IVb only on heating at 80°C for 3-4 h.

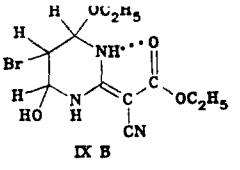
The addition products formed in acetic acid are unstable and on attempting to isolate them, they convert into 5-bromo-derivatives III, IVa, b. Contrary to this, dihydro-2-pyrimidinylidenecyanoacetic acid (IIa) in a mixture of chloroform with ethanol reacts with bromine at 20°C to form a mixture of fairly stable addition products VIII and IX, which can be separated chromatographically (see Table 1).



VIII



IX A

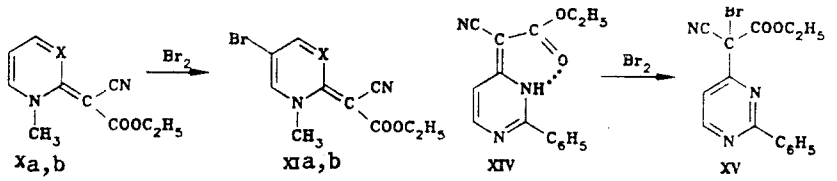


IX B

Compounds VIII and IX are colorless substances; their composition and structure conform with the elemental analysis data and spectral characteristics. In the PMR spectrum of compound VIII in $CDCl_3$ there are signals of the hexahydropyrimidine ring protons — at 4.83 (4,6-H) and 4.29 ppm (5-H) (compared with [8-10]), proton signals of two NH and three ethoxy groups (see Table 2). Hexahydropyrimidine IX is probably a product of the transformation

of compound VIII or of addition of H_2O and C_2H_5OH and bromination of the initial IIa. Its spectrum is more complex — two sets of proton signals are seen (see Table 2), which is clearly due to the possibility of the existence of two tautomeric compounds — IXA and IXB. On sublimation in vacuo or boiling in isopropanol, compounds VIII and IX completely convert into a mixture of 5-bromo-substituted IVa and the starting IIa.

The ease of formation of the addition products of type VIII and IX from compounds I, IIa, b, is probably due to their preferential existence in the ylidene form similarly to 2(1H)-pyridone and 2(1H)-pyrimidone [4, 5]. We confirmed this in two ways. Model N-methyl derivatives Xa, b by the action of bromine in CH_3COOH, possibly via the formation of analogous addition products, readily give 5-bromo-substituted XIa and XIb, respectively. 4-Pheny-2-pyrimidinylmalonic ester (XII), existing in solutions in the aromic form [7], and having no tendency to undergo addition reactions, is brominated under these conditions exclusively in the side chain giving the dimethyl ester of 4-phenyl-2-pyrimidinylbromomalonic acid (XIII).



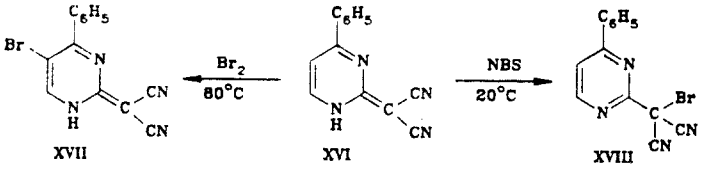
X, XI a X=CH; b X=N

The bromination of N-methyl-2-pyridone with bromine proceeds nonselectively and leads to the formation of a mixture of 3-bromo- and 3,5-dibromo-derivatives [11]. However, compounds I and Xa react with bromine exclusively at the 5-position, which is clearly due to steric hindrance at the 3-position. For the same reasons, the action of bromine in acetic acid at 20°C on dihydropyrimidine XIV does not lead to the bromination at the 5-position but to the formation of 2-phenyl-4-pyrimidinylbromocyanoacetic ester (XV). On further heating of the reaction mixture, only the splitting off of bromine takes place and the formation of the starting compound XIV. The phenyl groups at the 4,6-positions of dihydropyrimidine IIc also hinder entry of the bromine into the ring and, therefore, compound IIc is brominated at the exocyclic carbon atom with the formation of 4,6-diphenyl-2-pyrimidinylbromocyanoacetic ester (VIc).

These data show that the bromination in the side chain of compounds I and IIa, b proceeds fairly rapidly. However, the azinylbromocyanoacetic esters V and VIa, b formed are unstable under the reaction conditions (heating at 80°C in the presence of Br_2 and HBr) and convert into the thermodynamically more stable 5-bromo derivatives III and IVa, b (via the formation of the starting compounds I and IIa, b). This was shown by special experiments (see Experimental).

The reaction of dihydroazinylidenecyanoacetic esters I and IIa-c with N-bromosuccinimide in acetic acid at 20°C results after a few minutes in quantitative formation of the corresponding side-chain bromination products — 2-pyridyl-, 2-pyrimidinyl-, 4-pheny-2-pyrimidinyl-, and 4,6-diphenyl-2-pyrimidinylbromocyanoacetic esters (V, VIa, VIb, and VIc). Compounds V and VIa-c are stable under the reaction conditions, and judging from the TLC, the reaction mixtures do not contain ring-bromination products. Hence, under the kinetic control conditions, side-chain bromination products can be obtained.

4-Phenyl-1,2-dihydro-2-pyrimidinylidenemalononitrile (XVI) is considerably less soluble than compound IIb, which does not interfere with analogous transformations of compound XVI. By the action of bromine in DMFA at 80°C on compound XVI, 5-bromo-4-phenyl-1,2-dihydro-2-pyrimidinylidenemalononitrile (XVII) is formed, while by the action of NBS at 20°C, the side-chain bromination product [4-phenyl-2-pyrimidinylbromomalononitrile (XVIII)] is obtained.



The results of the bromination of the sodium salts of dihydro-2-pyrimidinylidenecyanoacetic esters IIa-c are also dependent on the reagent and the pH of the medium. In the reaction of bromine with the sodium salts of compounds IIa-c generated by the action of an equimolar amount of sodium hydride on dihydropyrimidines IIa-c in dimethoxyethane, a mixture of monobromo derivatives VIa-c and 2-pyrimidinyldibromoacetonitriles VIIa-c, respectively, is formed. The formation of dibromoacetonitriles VIIa-c is probably the result of decarboxylation of compounds VIa-c and their further bromination. The action of sodium hypobromite on the sodium salts of compounds IIa-c in an aqueous NaOH solution leads to the preferential formation of dibromo derivatives VIIa-c.

TABLE 2. PMR Spectra of Compounds III-IX, XIa, b, XIII, XV-XVIII

Compound	Chemical shifts, δ, ppm (in $CDCl_3$)							SSCC, J, Hz
	OCH_2CH_3, t*	OCH_2CH_3, q*	4-H	6-H	5-H	C_6H_5, m	other protons	
III	1,30	4,21	7,58 d. d	7,71d .d			7,20 (1H, d. d, 3-H); 14,01 (1H, d. d, NH)	$J_{34}=9,6$; $J_{61}=6,3$; J_{31}, $J_{46}=2,1$
IVb**	1,32	4,32		8,71 s		7,38 . .7,75	14,6 (1H, br. s, NH)	
V	1,26	4,28	7,87 d.d	8,54 d	7,34 t		7,48 (1H, d, 3-H);	$J_{45}=J_{56}=4,5$; $J_{34}=5,7$
VIa	1,27	4,39	8,84 d	8,84 d	7,41 t			J_{45}, $J_{56}=4,5$
VIb	1,26	4,36		8,73 d	7,69 d	7,36 . . . 7,59; 7,94 . . . 8,23		$J_{56}=5,0$
VIc	1,30	4,30			7,86 s	7,19 . . . 7,49; 7,89 . . . 8,16		
VIIa			7,95 d	7,95 d	7,80 t			J_{45}, $J_{56}=5,2$
VIIb***				8,99 d	7,36 . . . 7,66; 7,99 . . . 8,36			$J_{56}=5,1$
VIIc***					8,73	7,58 . . . 7,83; 8,53 . . . 8,63		
VIII	1,19; 1,23; 1,26	3,51; 3,71; 4,14	4,83 br. s	4,83 br. s	4,29 br . s		7,33 (1H, br. s, NH); 10,20 (1H, br . s, NH···O)	
IX	$1,22^{A+B}$; $1,26^{A+B}$	$3,56^{A(B)}$; $3,79^{B(A)}$; $4,16^{A+B}$	4,95 m, A+B	4,95 m, A+B	4,38 br .s A+B		4,51 (1H, s, OH)$^{A(B)}$; 4,57 (1H, s, OH)$^{B(A)}$; 7,17 (1H, br.s , NH)$^{A(B)}$; 7,74 (1H, br. s, NH)$^{B(A)}$; 10,14 (1H, br. s, NH···O)$^{A(B)}$; 10,32 (1H, br. s, NH···O) $^{B(A)}$	
XIa	1,34	4,21	8,21 d. d	8,64 d. d			7,74 (1H, d. d., 3-H); 3,61 (3H, s, N—CH_3)	$J_{34}=9,5$; J_{31}, $J_{46}=2,0$; $J_{61}=6,0$
XIb	1,34	4,24	7,83 d	8,43 d			3,69 (3H, s, N—CH_3)	$J_{46}=4,6$
XIII				9,01 d	7,20 . . . 7,78; 7,85 . . . 8,40		3,96 (6H, s, $2COOCH_3$)	$J_{56}=5,2$
XV	1,34	4,42		8,76 d	7,74 d	7,31 . . . 7,57; 8,27 . . . 8,61		$J_{56}=5,8$
XVI				7,70 d	6,87 d	7,32 . . . 8,15		$J_{56}=7,0$
XVII				8,56 s		7,28 . . . 7,70; 8,02 . . . 8,28		$J_{65}=5,0$
XVIII				8,79 d	7,32 . . . 7,85; 7,92 . . . 8,37			

*J = 7.0 Hz.

**Spectrum of the main tautomeric form.

***In DMSO-D_6.

TABLE 3. Bromination Conditions of Compounds I, IIa-c, Xa, b, XII, XIV, XVI, and Yields of Obtained Products

Starting compound	Method	Reaction product	Yield, %	Starting compound	Method	Reaction product	Yield, %
I	A	III	80	IIc	A	VIc	80
	E	V	95		B	VIc	85
IIa	A	IVa*	80		C	VIIc	80
	B	VIa	95		D	VIc	25
	C	VIIa	23			VIIc	50
	D	VIa	20	Xa	A	XIa	80
		VIIa	40	Xb	A	XIb	85
IIb	A	IVb	85	XII	A	XIII	85
	B	VIb	95	XIV	A	XV	90
	C	VIIb	80		B	XV	95
	D	VIb	24	XVI	A	XVII	85
		VIIb	46		B	XVIII	95

*The melting point (189-193°C) coincides with that given in [16].

The composition and structure of all the compounds obtained were confirmed by the analytical and spectral characteristics (see Tables 1 and 2). The 5-bromo derivatives III, IVa, b, XIa, b, and XVII, like the starting dihydroazines I, IIa, b, Xa, b, and XVI, existing in the ylidene form, are bright yellow crystalline substances. They are characterized by a long-wave absorption band in the UV spectra ($\lambda > 350$ nm). In the IR spectra of these compounds (besides the derivative XVII), the absorption band of the conjugated ester groups is located in the 1500-1700 cm^{-1} region ($\nu_{C=C}$, $\nu_{C=O}$), while the conjugated C≡N group appears at 2210 cm^{-1}. In the PMR spectra of these compounds, the 5-H signals of dihydroazine are absent. The bromo derivatives in the side chain (compounds V, VIa-c, XV, XVIII) contain a heteroaromatic ring, which is confirmed by the UV and PMR spectral data (see Tables 1 and 2). There are also proton signals of the ester group in the PMR spectra of these compounds, which appears in the IR spectra in the form of two absorption bands (1760 and 1780 cm^{-1}), clearly belonging to rotation isomers. Dibromoacetonitriles VIIa-c have in the PMR spectra proton signals only in the aromatic region (7.5-9.0 ppm.

We have thus selected conditions enabling the selective bromination of the ylidene derivatives of azines in yields higher than 80% and with a high regioselectivity, either into the 5-position of the azine ring or into the side chain. The corresponding anions are brominated into the side chain with the formation of mono- and dibromo-derivatives.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer in KBr tablets, the UV spectra on a Specord UV-VIS spectrophotometer in ethanol, and the PMR spectra on Varian A-56/60 (60 MHz) and Bruker WP-200 SY (200.13 MHz) spectrometers, using HMDS as the internal standard. The course of the reactions and the purity of the compounds obtained was monitored by TLC on Silufol UV-254 plates in a $CHCl_3$—C_2H_5OH (10:1) system.

The 1,2-dihydro-2-pyridilyline cyanoacetic ester (I) was synthesized according to [6], 1,2-dihydro-2-pyrimidinylidenecyanoacetic ester (IIa) — according to [2], 4-phenyl- IIb, and 4,6-diphenyl-substituted IIc derivatives according to [12]. The melting point of compound IIb coincides with that given in [7]. 4-Phenyl-2-pyrimidinylmalonic ester (XII) was obtained according to [7]. The N-methyl derivatives Xa, b were obtained in yields of 35-40% by methylation of the starting esters I and IIa with DMFA diethylacetal by a method analogous to that given in [13]. The melting points of products Xa, b correspond to those given in [3, 14]. 2-Phenyl-1,4-dihydro-4-pyrimidinylidenecyanoacetic ester (XIV) was obtained according to [3]. 4-Phenyl-1,2-dihydro-4-pyrimidinylidenemalononitrile (XVII) was synthesized in a yield of 79% from 4-phenyl-2-chloropyrimidine [15] by a method similar to that used in the preparation of 6-phenyl-4-chloro-1,2-dihydro-4-pyrimidinylidenemalononitrile [16].

The bromination conditions and yield of the obtained products are given in Table 3. The elemental analysis data for C, H, Br, N correspond to the calculated values.

General Methods of Bromination of Compounds I, IIa-c, Xa, b, XII, XIV, XVI. A. Bromination with Bromine in Acetic Acid. A solution of 0.31 ml (6 mmoles) of Br_2 in 10 ml of CH_3COOH was added dropwise to

a solution of compound I, IIa, b, Xa, b, XII in 20 ml of acetic acid, heated to 80°C. The mixture was heated for 3-4 h at 80°C (TLC monitoring of the disappearance of the starting compound). The acetic acid and excess of bromine were removed on a rotary evaporator (at 40°C), 5 ml of H_2O was added to the residue, the precipitate was filtered off, washed on the filter with H_2O (2 × 3 ml), dried in a vacuum desiccator, and the bromo derivatives III, IVa, b, XIa, b, and XVIII, respectively, were obtained.

For compound IIc the reaction with bromine proceeds at 20°C in 2 h without heating with the formation of product VIc, and for compound XIV in 48 h without heating with the formation of compound XV. On heating compounds IIc and XIV with bromine in acetic acid at 80°C for 3 h, with subsequent treatment of the reaction mixture as described above, the starting compounds IIc and XIV were recovered.

Because of its poor solubility, malononitrile XVI was brominated in a DMFA solution at 80°C for 3 h; the product XVII was isolated as described above.

B. Bromination with NBS in Acetic Acid. A 0.36 g portion (2 mmoles) of NBS was added to a solution of 2 mmoles of compounds I, IIa-c, XIV, and XVI in 20 m of CH_3COOH, and the mixture was stirred to decoloration (1-3 min), with TLC monitoring of the disappearance of the starting compound. The solution was evaporated on a rotary evaporator (at 40°C), 5 ml of H_2O was added to the residue, and the solution was decanted; the procedure was thrice repeated. The residue was dried in a vacuum desiccator. The oily products V and VIa were filtered through a layer of silica gel (a 3 × 5 cm column, eluent $CHCl_3$), and compounds VIb, c, XV, XVIII were recrystallized from ethanol.

Two to three drops of concentrated HBr were added to a solution of 1 mmole of the monobromo derivative VIa, b in 10 ml of CH_3COOH (to pH ~ 1) and the mixture was heated at 80°C for 3 h. The reaction mixture was evaporated on a rotary evaporator (at 40°C) and 5 ml of H_2O was added to the residue. The precipitate that separated out was filtered off, washed with 2 × 3 ml of H_2O, and dried in a vacuum desiccator over NaOH. Compound IVa (IVb, respectively) was obtained, which, as indicated by its melting point, was identical with samples obtained by method A.

C. Bromination of Na Salts of 1,2-Dihydro-2-pyrimidinylidenecyanoacetic Esters by Sodium Hypobromite. A solution of a Na salt of compounds IIa-c [prepared from 3.2 mmoles of IIa-c and 1.5 g (37.5 mmoles) of NaOH in 15 ml of water] was added to a solution of freshly prepared sodium hypobromite [from 0.33 ml (6.4 mmoles) of bromine, and 0.5 g (12.5 mmoles) of NaOH in 5 ml of water], cooled to 15°C. The reaction mixture was stirred at 20°C for 30 min to 2 h (TLC monitoring), acetic acid was added to pH 7, the precipitate was filtered off and washed with 5 × 3 ml of H_2O. The dibromoacetonitriles VIIa-c obtained were recrystallized from an ethanol—DMFA (5:1) mixture.

D. Bromination of Na Salts of 1,2-Dihydro-2-pyrimidinylidenecyanoacetic Esters by Bromine in Dimethoxyethane with Addition of DMFA. A solution of 0.05 ml (1 mmole) of bromine in 2 ml of dimethoxyethane was added dropwise to a suspension of 1 mmole of compound IIa-c and 0.033 g (1.1 mole) of an 80% dispersion of NaH in an oil in 3 ml of diemthxyethane, and then 0.5 ml of DMFA was added. The reaction mixture was stirred for 30 min to 1 h 30 min at 20°C (the disappearance of the starting compound was monitored by TLC). The solvents were distilled off on a rotary evaporator (at 40°C). To the residue 5 ml of cold water was added, the mixture was neutralized with acetic acid, the precipitate that separated out was filtered off, washed with 3 ml of H_2O, and dried in a vacuum desiccator. The mixture of products VIa-c and VIIa-c (according to the TLC data) was separated on a preparative scale on Silufol UV-254 plates (200 × 200 mm) in $CHCl_3$.

Bromination of 1,2-Dihydro-2-pyrimidinylidenecyanoacetic Ester (IIa) by Bromine in Chloroform. A solution of 1.4 ml (24 mmoles) of bromine in 15 ml of $CHCl_3$ was added dropwise in the course of 25 min to a solution of 228 g (12 mmoles) of compound IIa in 70 ml of chloroform (containing ~2% of ethanol). The suspension thus formed was stirred for 1 h at 20°C, the precipitate was filtered off, washed on the filter with 4 × 5 ml of $CHCl_3$, and dried in a vacuum desiccator. Thus, 2.2 g of a mixture of compounds VIII, IX, and IIa was obtained [according to TLC, R_f ~0.8, 0.6, and 0.4 (in chloroform), respectively], which was partitioned on a 2 × 180 cm column of silica gel; eluent $CHCl_3$. Yield 0.7 g (20%) of compound VIII, 0.8 g (25%) of compound IX, and 0.5-1 g of the starting compound IIa.

A solution of 50 mg of compound VIII (or IX) in 5 ml of isopropanol was boiled for 15 min. Judging from TLC, compound VIII (or IX) forms a mixture of IIa and IVa. In a similar way, heating of compounds VIII and IX in a sublimator (under an oil pump vacuum at 0.67 kPa) for 2 h leads to the formation of a mixture of compounds IIa and IVa (30 mg). According to the PMR data of the mixture, the ratio IIa:IVa is equal to 1:2.

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DIAZABICYCLOALKANES WITH NITROGEN ATOMS IN BRIDGEHEAD POSITIONS.

24.* SYNTHESIS AND REACTIONS OF BENZO[f]-1,5-DIAZABICYCLO[3.2.2]NONEN-3-ONE

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Benzo[f]-1,5-diazabicyclo[3.2.2]nonen-3-one was synthesized by the oxidation of benzo[f]-1,5-diazabicyclo[3.2.2]nonen-3-ol by dimethyl sulfoxide in the presence of N,N'-dicycohexylcarbodiimide and the reactions of this compound with 2,4-dinitrophenylhydrazine, phenylmagnesium bromide, and condensation with 4-nitro-benzaldehyde were carried out. It was shown that on heating with hydrobromic acid, benzo[f]-1,5-diazabicyclo[3.2.2]nonen-3-one undergoes dealkylation with the formation of 1,2,3,4-tetrahydroquinoxaline.

In continuation of the development of a method of synthesis of functional derivatives of benzodiazabicycloalkenes at the alicyclic part of the molecule, from the previously obtained benzo[f]-1,5-diazabicyclo[3.2.2]nonen-3-ol (I) we synthesized benzo[f]-1,5-diazabicyclo[3.2.2]nonen-3-one (II) and carried out a series of reactions characteristic for carbonyl compounds.

Various reagents were used for the oxidation of compound I at room temperature. On treatment with chromic anhydride in sulfuric acid and ammonium persulfate in various media, no oxidation reaction was observed. When

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