13. P. E. Hansen, Progress in Nuclear Magnetic Resonance Spectroscopy, Vol. 14, Part 4, Pergamon, Oxford (1981), p. 191.

REACTIONS OF N-ALKYLAZINIUM CATIONS. 3.* QUATERNARY PTERIDINIUM SALTS. SYNTHESIS, STRUCTURE, AND REACTIONS WITH SIMPLE NUCLEOPHILES

I. V. Kazantseva, V. N. Charushin, O. N. Chuapkhin, A. I. Chernyshev, and S. E. Esipov

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4-Morpholinopteridine reacts with triethyloxonium tetra-fluoroborate to give two types of isomeric quaternary salts, viz., 1-ethyl- and 8-ethyl-4-morpholinopteridinium tetrafluoroborates. The structures of the pteridinium cations were proved by the ^1H and ^{13}C NMR spectra and also by chemical transformations in reactions with simple nucleophiles.

The chemistry of pteridines has undergone significant development because of the important role of derivatives of this series in biochemical processes [2, 3]. Reactions of pteridines with diverse N, O, S, and C nucleophiles are known [2, 3], and the phenomenon of covalent hydration of protonated forms of the pteridinium ion has been studied thoroughly [4]; however, the literature contains no information regarding quaternary pteridinium salts or their reactions with nucleophiles.

The aim of the present research was to obtain quaternary N-alkylpteridinium salts and to study their structures and reactivities with respect to simple nucleophiles.

Considering the ease with which protonated forms of pteridine are hydrated in both the pyrimidine and pyrazine rings [5], the preparation of stable pteridinium cations seemed possible only when mesomeric-donor substituents, which participate in declocalization of the positive charge, are present. Alkoxy, alkylmercapto, or dialkylamino groups could have been substituents of this sort, since the alkylation of pteridines with free hydroxy and amino groups, even though it does take place at one of the ring nitrogen atoms, leads to uncharged oxo or imino derivatives as a result of deprotonation of these groupings [6, 7]. Starting from these premises and taking into account the fact that the pyrimidine ring, particularly the $C(_4)$ atom, is most vulnerable to the formation of covalent hydrates, in the present research we investigated the quaternization of 4-morpholinopteridine (I), which was obtained from 4-methylthiopteridine [8].

Since pteridines have low basicities and attempts to obtain quaternary salts by reaction with methyl iodide were unsuccessful [9], the quaternization of pteridine I was carried out with triethyloxonium tetrafluoroborate at 40°C in methylene chloride. Under these conditions 4-morpholinopteridine (I) forms two types of stable pteridinium salts with quaternary nitrogen atoms in the 1 (II) and 8 (III) positions, which were synthesized preparatively in 77% and 8% yields, respectively (Tables 1 and 2). It is known [3] that the basicities of the nitrogen atoms in unsubstituted pteridine decrease in the order $N_3 > N_1 > N_5 > N_8$. It is therefore not surprising that alkylation of the sterically accessible and more basic N_1 atom of the pyrimidine ring as compared with the N_8 atom of the pyrazine ring is the preferred quaternization pathway.

*See [1] for communication 2.

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TABLE 1. Characteristics of Pteridines I-III and VIa-d

Compound	mp, deg C	R_f*		Found			Empirical formula	Calculated			Yield, %
		A	B	C	H	N (S)		C	H	N (S)	
I	173—175	0,37	0,26	55,1	5,1	32,2	$C_{10}H_{11}N_5O$	55,3	5,1	32,2	70
II	149—152	—	—	43,2	4,8	21,4	$C_{12}H_{16}N_5OBF_4$	43,3	4,8	21,0	77
III	164—168	—	—	43,1	4,6	21,4	$C_{12}H_{16}N_5OBF_4$	43,2	4,8	21,0	8
VIa	237—239	0,43	0,65	59,1	3,5	37,8	$C_{11}H_8N_6$	58,9	3,6	37,5	97
VIb	228—230	0,46	0,63	57,0	4,9	25,2	$C_{13}H_{13}N_5O_2$	57,6	4,8	25,8	80
VIc	298—301	0,11	0,25	55,1	4,2	34,5	$C_{11}H_{10}N_6O$	54,5	4,2	34,7	62
VId	240—242	0,22	0,41	51,4	4,1	32,8 (12,4)	$C_{11}H_{10}N_6S$	51,2	3,9	32,5 (12,4)	61

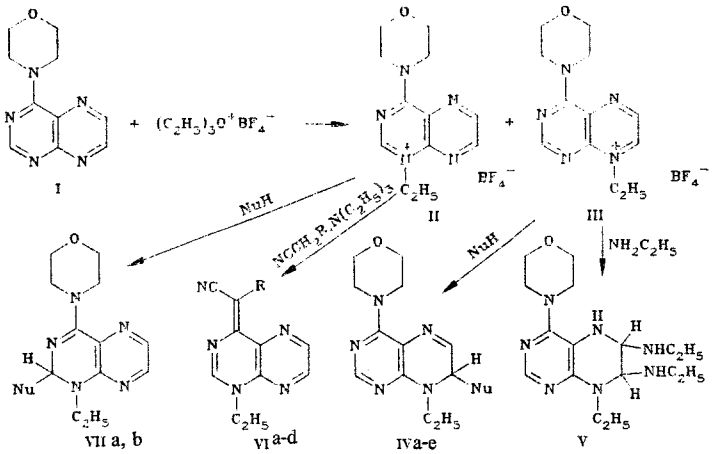
*System A was chloroform—ethyl acetate—ethanol (6:3:1), and system B was chloroform—acetone (1:1).

TABLE 2. Characteristics of the ^1H NMR Spectra of 4-Morpholinopteridine (I) and Isomeric Quaternary Salts II and III in d_6-DMSO

Compound	Chemical shifts, δ, ppm						$^3J_{6,7}$, Hz
	2-H	6-H	7-H	morpholine ring protons		$\overset{+}{N}-C_2H_5$	
				$O(CH_2)_2$	$N(CH_2)_2$		
I	8,66 s	8,82 d	9,06 d	3,78 m	4,40 m	—	1,9
II	9,13 s	9,11 d	9,19 d	3,86 m	4,36 m (2H); 4,97 m (2H)	1,45 t (3H); 4,54 q (2H)	2,1
Δ(II—I)	0,47	0,29	0,13	0,08	−0,04; 0,57		0,2
III	8,80 s	9,30 d	9,48 d	3,82 m	4,30 m (2H); 4,70 m (2H)	1,35 t (3H); 4,90 q (2H)	3,0
Δ(III—I)	0,14	0,48	0,42	0,04	−0,10; 0,30		1,1

The structures of quaternary pteridinium salts II and III were established on the basis of data from the ^1H and ^{13}C NMR spectra (Tables 2 and 3 and Figs. 1 and 2) and were also confirmed by their chemical transformations in reactions with nucleophilic reagents.

The data in Table 2 makes it possible to follow the changes in the characteristics of the ^1H NMR spectra of 4-morpholinopteridine (I) as a result of quaternization.



IV, VII a Nu=OCH_3; b Nu=$N(C_2H_5)_2$; c Nu=OH; d Nu=$CH(CN)_2$; e Nu=HNC_2H_5; VI a R=CN; b R=$COOC_2H_5$; c R=$CONH_2$; d R=$CSNH_2$

The greatest shift of the singlet signal of the 2-H proton to weak fields on passing from base I to salt II (Δ = 0.47 ppm) indicates quaternization of the N_1 atom of the pyrimidine. The doublet signals of the 6-H and 7-H protons of the pyrazine ring, which are in the para and meta positions relative to the ammonium grouping, are also shifted to weak field

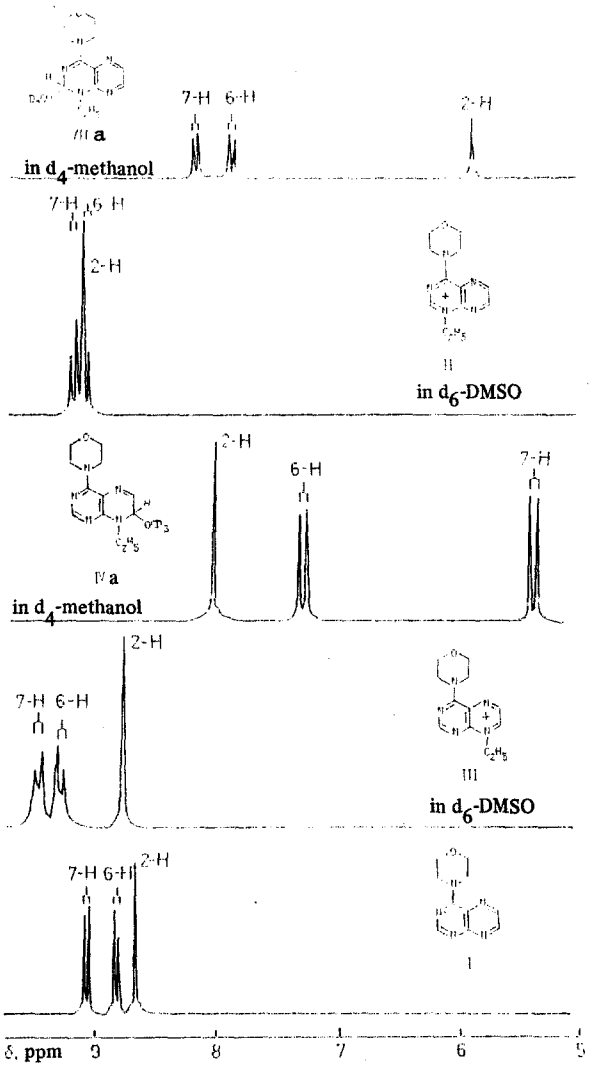


Fig. 1. ^{1}H NMR spectra of 4-morpholinopteridine (I), isomeric quaternary salts II and III (in d_6-DMSO), and their methoxy adducts IVa and VIIa (in d_4-methanol).

but to a considerably smaller extent, viz., 0.29 and 0.13 ppm, respectively (Table 2 and Fig. 1). For III, on the other hand, greater shifts to weak field of the doublet signals of the 6-H and 7-H protons of the pyrazine ring (Δ = 0.48 and 0.42 ppm, respectively) are observed, whereas the singlet signal of the 2-H proton is shifted only 0.14 ppm (Table 2 and Fig. 1). Quaternization of the N_8 atom in III is also confirmed by the increase in the SSCC of the protons of the pyrazine ring ($^3J_{6,7}$) from 1.9 Hz (pteridine I) to 3.0 Hz (the III cation); as noted in a study of the quaternization of pyrido[2,3-b]pyrazines [10], this is one of the diagnostic signs in the determination of the quaternization center.

All of the characteristics of the ^{13}C NMR spectra of isomeric quaternary salts I and III also correspond to their structures. The assignment of the signals in the ^{13}C NMR spectrum of pteridine I (Table 3 and Fig. 2) was made on the basis of literature data [11] on the chemical shifts of unsubstituted pteridine and related compounds and with allowance for the multiplicities of the signals and the values of the ^nJ(C–H) constants in the ^{13}C NMR spectra recorded without spin-spin decoupling of the protons. The mutual assignment of the signals in the ^{1}H and ^{13}C NMR spectra was made on the basis of experiments involving selective decoupling of the coupling of the 2-H, 6-H, and 7-H protons with the ^{13}C nuclei. The doublet-doublet signals at δ 141.89 and 150.40 ppm are related to the methylidyne $C_{(6)}$ and $C_{(7)}$ atoms of the pyrazine ring, and the doublet signal at 157.54 ppm is related to the $C_{(2)}$ atom of the pyrimidine fragment. Of the three signals of quaternary carbon atoms, the strongest-field (128.12 ppm) doublet signal with $^3J[C_{(4a)}–H_6]$ = 11.2 Hz is related to the $C_{(4a)}$ atom, which is bonded only to one nitrogen atom. The signal at 155.19 ppm shows up

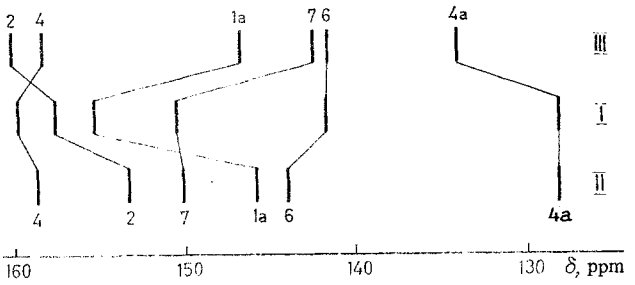


Fig. 2. Diagram of the changes in the chemical shifts in the ^{13}C NMR spectra in d_6-DMSO on passing from 4-morpholino-pteridine (I) to quaternary salts II and III.

in the form of a double doublet with ^3J = 12.3 and 13.6 Hz and is related to the $C_{(1a)}$ atom. The signal of the $C_{(4)}$ atom shows up at 159.73 ppm in the form of a double multiplet due to coupling with the 2-H proton (^3J = 10.6 Hz) and four N-methylene protons of the morpholino substituent (Table 3).

The assignments of the signals in the ^{13}C NMR spectra of quaternary salts II and III were similarly made (Table 3 and Fig. 2). Considering the closeness of the singlet and doublet signals of the resonance of the 2-H and 6-H protons in the PMR spectrum of salt II (the difference in the chemical shifts in 0.02 ppm), experiments involving the observation of the ^{13}C resonance with selective spin-spin decoupling of the protons were carried out at a low reduced power of the decoupling apparatus ($\gamma H_2/2\pi \approx 400$ Hz). In the case of irradiation of a sample of II with a frequency corresponding to the resonance of the 2-H proton (9.13 ppm) the signal of the $C_{(2)}$ atom shows up in the form of a triplet with a residual constant due to coupling with the methylene protons of the N-ethyl group. The $C_{(7)}$ and $C_{(6)}$ signals in this case were recorded in the form of doublets with residual $^1J_{res}$ constants due to coupling with the 7-H and 6-H protons. Similar experiments involving the decoupling of the 7-H (9.19 ppm) and 6-H (9.11 ppm) protons led to distinct singlets of the $C_{(7)}$ and $C_{(6)}$ signals, respectively. Measurement of the long-range SSCC for the bridge $C_{(1a)}$ atom was hindered because of overlapping of the signal of the $C_{(1a)}$ atom and the strong-field doublet component of the $C_{(7)}$ signal.

Two markedly broadened signals ($\Delta\nu_{1/2} \approx 10$ Hz) of quaternary (146.70 ppm) and methylidyne (142.39 ppm) carbon atoms are observed in the ^{13}C NMR spectrum of III. In [10] it was shown that quaternization of pyrido[2,3-b]pyrazines leads to marked broadening of the signals of the α-carbon atoms. On the basis of this the above-indicated signals of quaternary salt III were assigned, respectively, to the $C_{(1a)}$ and $C_{(7)}$ atoms. The assignment of the signals of the methylidyne fragments of the heterocyclic system was made on the basis of experiments with selective decoupling of the coupling of the protons with the ^{13}C nuclei. Because of marked broadening and mutual overlapping of the signals in the ^{13}C NMR spectra of salt III recorded without suppression of the spin-spin coupling with the protons we were unable to measure the long-range SSCC for the $C_{(1a)}$ and $C_{(4a)}$ atoms; the ^1J constants for the $C_{(6)}$ and $C_{(7)}$ atoms were measured with an accuracy of ± 1 Hz.

It is known [10, 12] that quaternization of azines leads to a 6-10 ppm shift to strong field of the signals of the α-carbon atoms in the ^{13}C NMR spectra. The observed 9.35 and 4.31 ppm shifts to strong field of the $C_{(1a)}$ and $C_{(2)}$ signals in the ^{13}C NMR spectrum of II with respect to base I indicate quaternization of the $N_{(1)}$ atom. The conclusion regarding quaternization of the $N_{(8)}$ atom similarly follows on the basis of the shifts of the $C_{(1a)}$ and $C_{(7)}$ signals in the ^{13}C NMR spectrum of III with respect to I (Table 3 and Fig. 2). The increase in the absolute values of the $^1J_{(C-H)}$ constants for the pyrimidine (II) and pyrazine (III) rings by more than 10 Hz (Table 3) is yet another piece of evidence [10] for the quaternization of the $N_{(1)}$ and $N_{(8)}$ atoms, respectively.

The ^1H and ^{13}C NMR spectra also indicate that structure IIb with a $C_4{=}N$ double bond makes a significant contribution to stabilization of the II cation. Retarded (on the NMR time scale) rotation about the $C_4{-}N$ bond is manifested in the presence of two signals of $N{-}CH_2$ groups in the ^1H and ^{13}C NMR spectra of II. By selective decoupling of the spin-spin coupling of the $N{-}CH_2$ protons with shifts of 4.36 and 4.97 ppm we demonstrated their coupling

TABLE 3. Effect of Quaternization of 4-Morpholinopteridine (I) at the $N_{(1)}$ and $N_{(8)}$ Atoms on the ^{13}C Chemical Shifts and the $^{n}J(C-H)$ Constants (Hz) in the ^{13}C NMR Spectra in d_6-DMSO

Compound	δ, ppm								^1J			^2J		^3J					
	$C_{(2)}$	$C_{(4)}$	$C_{(6)}$	$C_{(7)}$	$C_{(1a)}$	$C_{(4a)}$	$O(CH_2)_2$	$N(CH_2)_2$*	C_2-H_2	C_6-H_6	C_7-H_7	C_8-H_7	C_7-H_8	$C_1 H_2$	$C_4-N(CH_2)_2$	$C_{(1a)}-H_2$	$C_{(1a)}-H_7$	$C_{(4a)}-H_6$	C_2-NCH_2
I	157,54	159,73	141,89	150,40	155,19	128,12	66,37	47,96	199,7	188,1	185,2	11,0	11,6	10,6	— †	12,3‡	13,6‡	11,2	—
II	153,23	158,58	144,14	150,22	145,84	127,97	66,41	48,50; 50,74	213,4	192,3	190,8	10,8	11,3	11,0	— †	— †	—†	10,8	5,1
Δ(II—I)	−4,31	−1,15	2,25	−0,18	−9,35	−0,15	0,04	0,54; 2,78	13,7	4,2	5,6	−0,2	−0,3	0,4				−0,4	
III	160,13	158,31	141,85	142,39	146,70	133,96		48; 50	206,0	199,0	198,0							11,8	
Δ(III—I)	2,59	−1,42	−0,04	−8,01	−8,49	5,84			6,3	10,9	12,8							0,6	
Pteridine [11]	159,5	164,1	148,4	153,0	154,4	135,3			206,0	188,0	186,0								

*The two markedly broadened signals, which are mutually overlapped due to rapid exchange, are presented for III.
†The measurement of the constants was hindered because of overlapping of the signals (see the text).
‡One of the two indicated values.

TABLE 4. PMR Spectra of the Covalent Adducts of Pteridinium Salts with Water, Methanol, Ethyl- and Diethylamines, and Malonodinitrile

Adduct	Formation conditions*		Chemical shifts, δ, ppm			$^3J_{6,7}$, Hz
	reagents	solvent	2-H, s	6-H, d	7-H, d	
IVa	III + $N(C_2H_5)_3$, 1 : 1	CD_3OD	8,08	7,36	5,49	3,2
IVb	III + $NH(C_2H_5)_2$, 1 : 1	d_6-DMSO	6,94	6,18	4,05	3,1
IV†	III	D_2O	8,15	7,56	5,72	3,3
IVc	III + $N(C_2H_5)_3$, 1 : 1	D_2O	8,15	7,56	5,72	3,3
IVd	III + $CH_2(CN)_2$ + $N(C_2H_5)_3$, 1 : 1 : 1	d_6-DMSO	7,97	7,19	4,72	3,6
IVe†	III + $H_2NC_2H_5$, 1 : 3	d_6-DMSO	7,99	7,17	4,97	3,3
V‡	III + $H_2NC_2H_5$, 1 : 3	d_6-DMSO	7,85	5,18	4,83	—
VIIa	II + $N(C_2H_5)_3$, 1 : 1	CD_3OD	5,95	8,26	7,95	2,8
VIIb	II + $HN(C_2H_5)_2$, 1 : 1	$CDCl_3$	6,00	8,02	7,69	2,9

*At 35°C, except for adducts VIIa,b, which were detected at −40°C.

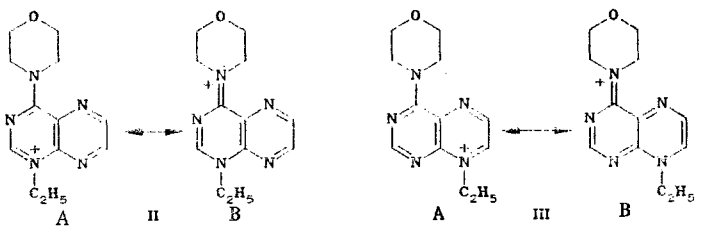
†The amount of adduct IVc in the equilibrium mixture with the III cation was 40%. Complete conversion was observed in the remaining cases.

‡A mixture of ethylamine IVe and diadduct V in a ratio of 3:1 was formed.

TABLE 5. Characteristics of the ^1H NMR Spectra of Pteridines VIa-d

Compound	Solvent	Chemical shifts, δ, ppm			
		2-H	6-H & 7-H	$N-C_2H_5$	R
VIa	d_6-DMSO − $CDCl_3$, 1 : 1	8,59 s	8,90 s (2H)	4,40 q (2H); 1,46 t (3H)	—
VIb	CF_3COOH	8,91 s	8,67 d, 8,71 d (J = 2 Hz)	4,38 q (2H); 1,28 t (3H)	4,15 q (2H); 1,09 t (3H)
VIc	d_6-DMSO	8,43 s	8,78 s (2H)	4,24 q (2H); 1,35 t (3H)	9,12 br. s (2H)
VId	d_6-DMSO	8,51 s	8,81 s (2H)	4,23 q (2H); 1,36 t (3H)	9,70 br. s (2H)

with the methylene carbon atoms, the signals of which are recorded at 48.50 and 50.74 ppm, respectively (Tables 2 and 3). An increase in the temperature of the sample to 112°C leads to coalescence of the signals of the protons of the $N(CH_2)$ groups in the ^1H NMR spectrum of II at 4.7 ppm. The frequency of rotation of the morpholino substituent at this temperature, which was evaluated from the equation $K = \sqrt{2}\pi\Delta\nu$, is greater than $2 \cdot 10^2$ Hz.



The contribution of resonance structure IIIB is less significant for isomeric salt III. In the ^1H and ^{13}C NMR spectra of III at 30°C the protons and carbon atoms of the $N-CH_2$ groups are recorded in the form of broad mutually overlapped signals. This constitutes evidence for intermediate (on the NMR time scale) exchange rates due to rotation of the morpholino substituent about the C_4-N bond. The weaker-field [as compared with the II cation (δ 4.54 ppm)] chemical of the methylene protons of the quaternary N-ethyl group (δ 4.90 ppm) also indicates the smaller contribution of resonance structure IIIb.

Not only the spectral characteristics of quaternary salts II and III but also their reactivities with respect to simple nucleophiles differ. Thus 1-ethyl-4-morpholinopteridinium ion (II) does not undergo covalent hydration, whereas 8-ethyl-4-morpholinopteridinium ion (III) adds water in the 7 position in the absence of a base to give σ adduct IVc; the ratio of the III cation to covalent hydrate IVc is 3:2. In the presence of triethylamine the III cation undergoes complete hydration to give stable adduct IVc. The 4.76-ppm shift to strong field of the signal of the pyrazine 7-H proton (d, J = 3 Hz) as compared with the III cation indicates the formation of σ adduct IVc, whereas the signals of the 2-H (s) and 6-H (d, J = 3 Hz) protons are shifted only 0.65 and 1.74 ppm, respectively, to strong field (Table 4). Similar changes in the ^{1}H NMR spectra are also observed in the formation of the adduct of salt III with methanol (Table 4 and Fig. 1). The chemical shifts and SSCC of dihydropteridines IVa,c are in good agreement with the data from ^{1}H NMR spectra of the adducts of the 1-methylquinoxalinium cation with water and methanol [13]. Adducts of the III cation with diethylamine (IVb) and malonodinitrile (IVd) were also detected by ^{1}H NMR spectroscopy (Table 4). In comparing the reactivity of pteridinium cation III with other 1,4-diazinium salts, particularly with the quinoxalinium cation, it should be noted that the III cation is, on the one hand, more electrophilic, since it, in contrast to the quinoxalinium cation, is hydrated by water in the absence of a base, whereas, on the other hand, the pteridinium cation has little inclination to form diadducts involving the pyrazine ring, which is characteristic for the quinoxalinium salt [13, 14]. A product of diaddition of a nucleophile to the III cation in the 6 and 7 positions was detected only in the reaction of ethylamine (diadduct V), and this diadduct was mixed with monoadduct IVe (Table 4).

The reactions with O, N, and C nucleophiles such as alcohols, amines, and CH-active compounds proceed via a different pathway in the case of quaternary salt II. The products of addition of methanol and diethylamine (VIIa,b) in the 2 position of the II cation are unstable and are detected in the ^{1}H NMR spectra only at reduced temperatures (from −40 to 0°C) (Table 4 and Fig. 1). A 9.13 to 5.95-ppm shift of the singlet signal of the 2-H proton to strong field is observed when salt II is dissolved in d_4-methanol in the presence of triethylamine at −40°C; the doublets of the protons of the pyrazine ring undergo only a small shift to strong field (Table 4 and Fig. 1). A σ adduct of salt II with the malonodinitrile carbanion would not be detected even at −40°C, since replacement of the morpholine residue to give pteridine VIa takes place very rapidly even under these conditions. Product VIa was also obtained when this reaction was carried out at room temperature. Products with a structure similar to that of VIb-d were also formed in the reaction of salt II with cyanoacetic ester, cyanothioacetamide.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded with Perkin-Elmer R-12B (60 MHz) and Bruker WH-90 (90 MHZ) spectrometers. The chemical shifts were measured on the δ scale with respect to tetramethylsilane (TMS) (δ_{TMS} = 0.00 ppm) and hexamethyldisiloxane (HMDS) (δ_{HMDS} = 0.05 ppm) internal standards for solutions in organic solvents and with respect to sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) (δ_{DSS} = 0.015 ppm) as the internal standard for D_2O solutions. The ^{13}C NMR spectra (4-10% solutions in d_6-DMSO) were recorded with a Bruker WH-90 spectrometer (22.62 MHz) at 30°C. The chemical shifts were measured on the δ scale relative to the signal of the solvent (δ_{DMSO} = 39.7 ppm). The numerical resolution was 0.5 Hz per point, which corresponded to the accuracy in the measurement of the chemical shifts (0.02 ppm) and the SSCC [$J_{(C-H)}$ = 0.5 Hz]. Experiments involving selective decoupling of the coupling of the protons with the ^{13}C nuclei were carried out at a reduced power of the decoupling apparatus ($\gamma H_2/2\pi \approx 400$ Hz).

The characteristics of the synthesized compounds are presented in Tables 1-3 and Table 5.

4-Morpholinopteridine (I). A mixture of 5 g (84 mmole) of 4-methylthiopteridine [8] and 16.5 ml (189 mmole) of morpholine in 125 ml of ethanol was refluxed for 24 h, after which it was cooled, and the precipitate was removed by filtration and recrystallized from ethanol to give 5.2 g (70%) of a product with mp 173-175°C.

Quaternization of 4-Morpholinopteridine. A solution of 4.5 g (23 mmole) of triethyloxonium tetrafluoroborate in 10 ml of methylene chloride was added to a solution of 4 g (18 mmole) of 4-morpholinopteridine in 40 ml of methylene chloride, and the mixture was refluxed for 3 h. The precipitated 8-ethyl-4-morpholinopteridinium tetrafluoroborate (III) was removed by filtration and recrystallized twice from absolute ethanol to give 0.45 g (8%) of

salt III with mp 164-168°C. The filtrate was evaporated to dryness, and the residue was recrystallized from absolute ethanol to give pteridinium tetrafluoroborate II. The yield of salt II, with mp 149-152°C, was 4.3 g (77%).

1,4-Dihydro-4-dicyanomethylene-1-ethylpteridine (VIa). A 0.2-g (3 mmole) sample of malonodinitrile and 0.83 ml (6 mmole) of triethylamine were added with stirring to a suspension of 1 g (3 mmole) of pteridinium tetrafluoroborate II in 15 ml of ethanol. Heating up of the reaction mixture, dissolving of the starting salt, and the formation of a yellow crystalline precipitate were observed as the triethylamine was added. The mixture was cooled, and the precipitate was removed by filtration, recrystallized from ethanol, and air dried to give 0.65 g (97%) of VIa with mp 237-239°C.

Compounds VIb-d were similarly obtained by reaction of the II cation with cyanoacetic ester, cyanoacetamide, and cyanothioacetamide.

LITERATURE CITED

1. V. N. Charushin, O. N. Chupakhin, G. M. Petrova, E. O. Sidorov, N. A. Klyuev, and L. G. Egorova, Khim. Geterotsikl. Soedin., No. 2, 255 (1981).
2. D. T. Hurst (editor), An Introduction to the Chemistry and Biochemistry of Pyrimidines, Purines, and Pteridines, Wiley, New York—London (1980).
3. W. Pfleiderer (editor), Chemistry and Biology of Pteridines, deGruyter, Berlin—New York (1975).
4. A. Albert, in: Advances in Heterocyclic Chemistry, Vol. 20, edited by A. R. Katritzky and A. J. Boulton, Academic Press, New York (1976), p. 117.
5. A. Albert, T. J. Batterham, and J. J. McCormack, J. Chem. Soc., B, No. 11, 1105 (1966).
6. W. Pfleiderer and M. Rukwied, Chem. Ber., 94, 118 (1961).
7. D. J. Brown and N. W. Jacobsen, J. Chem. Soc., No. 10, 4413 (1961).
8. A. Albert, D. J. Brown, and H. C. S. Wood, J. Chem. Soc., No. 11, 3832 (1954).
9. A. Albert, D. J. Brown, and H. C. S. Wood, J. Chem. Soc., No. 7, 2066 (1956).
10. O. N. Chupakhin, V. N. Charushin, A. I. Chernyshev, and S. E. Esipov, Magn. Reson. Chem., No. 4 (1985).
11. J. P. Geerts, A. Nagel, and H. C. van der Plas, Org. Magn. Reson., 8, 607 (1976).
12. R. J. Pugmire and D. M. Grant, J. Am. Chem. Soc., 90, 697 (1968).
13. J. W. Bunting and M. G. Meathrel, Can. J. Chem., 50, 917 (1972).
14. V. N. Charushin, M. G. Ponizovskii, O. N. Chupakhin, E. O. Sidorov, and I. M. Sosonkin, Khim. Geterotsikl. Soedin., No. 5, 669 (1985).