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DERIVATIVES OF OCTAHYDROPYRROLO[4,3,2-*m,n*]-ACRIDINE.
5.* ALKYLATION OF 1-METHYL AND 1-ARYL-4,4,8,8-TETRAMETHYL-2,3,4,5,7,8,9,10-OCTAHYDRO-PYRROLO[4,3,2-*m,n*]ACRIDIN-10-ONES

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*4,4,8,8-Tetramethyl-2,3,4,5,7,8,9,10-octahydropyrrolo[4,3,2-*m,n*]acridin-10-ones were alkylated at the nitrogen atom of the pyrrole ring by successive treatment with sodium hydride and an alkyl halide. Treatment of the neutral molecule with methyl iodide gave alkylation at the nitrogen atom of the pyridine ring. Derivatives of pyrrolo[4,3,2-*m,n*]acridine with no substituent at position 2 readily lost a proton from the NH group of the pyrrole ring to give bipolar structures.*

Previously the synthesis of 1-aryl-4,4,8,8-tetramethyl-2,3,4,5,7,8,9,10-octahydropyrrolo[4,3,2-*m,n*]acridin-10-ones [1], their ability to quench chemically generated singlet oxygen [2, 3], their antioxidant and antiradical activity, and their membranotropic properties [3] have been studied. The objective of the present work was to study the alkylation of derivatives of pyrroloacridine.

Because of the basicity of the nitrogen atom in the pyridine ring, pyrrolo[4,3,2-*m,n*]acridines III readily form hydrochlorides III [1]. Treatment of pyrroloacridines (II) with methyl iodide gave brightly colored pyrrolo[4,3,2-*m,n*]acridinium iodides (IV) (Table 1). The reaction occurs best with an excess of methyl iodide without an additional solvent. The reaction with propyl iodide proceeds poorly.

Dissociation of the NH bond in derivatives of pyrroloacridines II occurs under comparatively vigorous conditions (the pK_a of compounds IIb, IIc, and IId are 13.2, 16.5, and 11.3, respectively). However the reactions of pyrroloacridinium iodides IV with aqueous ammonia leads to the loss of the proton and the formation of a bipolar compound V as indicated by the sharp deepening of the color, which is characteristic of the anions of compounds II [1]. The structures of the betaines V resemble that of the known deep violet alkaloid cryptolepin (5-methyl-5H-indolo[3,2-*b*]quinoline) [4], i.e., compounds V may be described as derivatives of 6H-indolo[4,3-*a*,3-*b,c*]quinoline. In the crystalline state the deep violet (Va-c) or violet red (Vd, e) compounds are stable, but in dilute ethanol solution they have UV spectra close to those of the iodides IV, i.e., compounds V are solvated with a reversible change in their electronic structures. Addition of ammonia to these solutions causes a sharp bathochromic shift consequent on a return to structure V (Table 2). The similarity in structures of IV and V is shown for example by the observation that iodide IVc simultaneously forms two types of crystal, one red and the other violet, which have identical elemental analyses and UV spectra in ethanol solution.

The color of compounds V suggests the presence of a bipolar betaine structure. However, the excellent solubility of these compounds in chloroform and also the circumstance that the chemical shifts of the protons of the 5-CH_2 and 7-CH_2 groups in the ^1H NMR spectra are shifted to the weaker field only in the cases of the pyrroloacridinium chlorides III and the pyrroloacridinium iodides IV and VIII, but not in the spectra of the betaines V (Table 3), probably indicates intramolecular charge transfer. The unsuccessful attempts to alkylate the betaines V with methyl iodide are in agreement with this. The expected alkylation products VIIIa, b were obtained by retrosynthesis. As noted above, the betaines V are stable in the solid state and contain water of crystallization which is difficult to remove completely. In solutions a slow change in color is observed which indicates chemical change and this sharply limits the possibility of recrystallizing these compounds.

*For Communication 2, see [1]; for Communications 3 and 4, see [2, 3].

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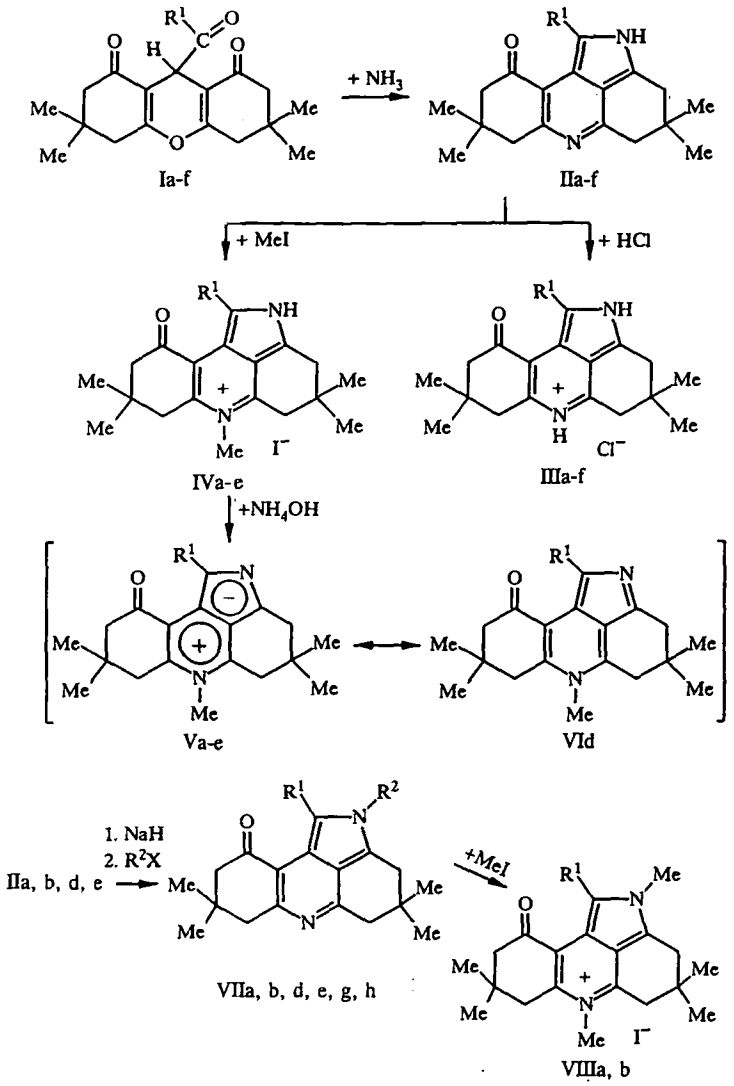

Ia—Va, VIIIa R^1 = Me; Ib—Vb, VIIIb R^1 = Ph; Ic—Vc R^1 = *p*-MeOC$_6$H$_4$;
Id—IVd, VId R^1 = *p*-O$_2$NC$_6$H$_4$; Ie—Ve R^1 = *m*-O$_2$NC$_6$H$_4$; If—IIIf R^1 = *p*-NCC$_6$H$_4$;
VIIa R^1 = R^2 = Me; VIIb R^1 = Ph, R^2 = Me; VIId R^1 = *p*-O$_2$NC$_6$H$_4$, R^2 = Me;
VIIe R^1 = *m*-O$_2$NC$_6$H$_4$, R^2 = Me; VIIg R^1 = *p*-O$_2$NC$_6$H$_4$, R^2 = $CH_2CH_2CH_3$;
VIIh R^1 = Ph, R^2 = $CH_2CH_2CH(CH_3)_3$; X = Cl, Br, I

The UV spectra of the chlorides III and the pyrroloacridinium iodides IV provided interesting material. In both cases the color of the compound deepened when an electron donating substituent R^1 was introduced. In all of the compounds II studied, alkylation at position 6 (iodides IV) or formation of the chlorides (salts III) led to a bathochromic shift in the UV spectrum. The only exceptions were the *p*-nitrophenyl substituted compounds IIId [1] and IVd in which a hypsochromic shift was observed in the UV spectra. A decrease in intensity of the shoulder on the long-wave length maximum in the case of salt IIId showed only a partial hydrolysis in solution, whereas in the case of the iodide IVd it indicated some equilibrium with the betaine Vd. Since coplanarity [5], and consequently conjugation of the 1-aryl substituent with pyrroloacridine system, is excluded, only an inductive effect of R^1 can occur. The reason for the qualitative difference observed in the UV spectra of pyrroloacridines with R^1 = *p*-$C_6H_4NO_2$ is probably the shift of the electron density in the 2H-pyrrolo[4,3,2-*m*,*n*]acridine system to convert it into 6H-pyrrolo[4,3,2-*m*,*n*]acridine. Evidently the positive charge in compounds IIId and IVd is shifted to the pyrrole ring and in the case of betaine Vd one can speak of the completely neutral structure VId.

Alkylation of compound II at the pyrrole nitrogen atom occurs on reaction of alkyl halides with the sodium salt of pyrroloacridine II, obtained by treatment with sodium hydride in an anhydrous solvent. Formation of compounds VII occurs very easily with methyl iodide, with more difficulty with alkyl bromides and chlorides. More vigorous conditions are needed with longer chains. The reaction did not occur with 2-iodopropane.

TABLE 1. Characteristics of Derivatives of Pyrrolo[4,3,2-*m,n*]acridine II-VIII

Compound	Molecular formula	(Found, %) / (Calculated, %) C	H	N	mp., °C	Yield, %
IIe*	$C_{24}H_{25}N_3O_3 \cdot 2H_2O$	65,20 / 65,59	6,48 / 6,65	9,33 / 9,56	259...261 (dec.)	65
IIf	$C_{25}H_{25}N_3O \cdot 2H_2O$	71,61 / 71,58	6,95 / 6,97	10,00 / 10,02	179...180	53
IIIa	$C_{19}H_{24}N_2O \cdot HCl \cdot C_2H_5OH$	66,55 / 66,56	8,31 / 8,25	7,25 / 7,39	>250 (dec.)	85
IIIc †	$C_{25}H_{28}N_2O_2 \cdot HCl \cdot 1/2H_2O$	69,58 / 69,19	7,07 / 6,98	6,33 / 6,45	>250 (dec.)	70
IVa	$C_{20}H_{27}IN_2O$	54,78 / 54,80	6,32 / 6,21	6,16 / 6,39	>250 (dec.)	74
IVb	$C_{25}H_{29}IN_2O \cdot 1/2H_2O$	58,99 / 58,94	5,81 / 5,94	5,50 / 5,50	>250 (dec.)	62
IVc	$C_{26}H_{31}IN_2O_2$	58,90 / 58,87	5,95 / 5,89	5,17 / 5,28	284...286 (dec.)	68
IVd	$C_{28}H_{28}IN_3O_3 \cdot 1/2H_2O$	54,34 / 54,16	5,24 / 5,27	7,39 / 7,58	>285 (dec.)	70
IVe †	$C_{28}H_{28}IN_3O_3 \cdot 1/2H_2O$	54,44 / 54,16	5,13 / 5,27	7,56 / 7,58	273...275 (dec.)	52
Va †	$C_{20}H_{26}N_2O \cdot H_2O$	73,34 / 73,36	8,17 / 8,31	8,49 / 8,55	‡	71
Vb †	$C_{25}H_{28}N_2O \cdot 1/2H_2O$	78,62 / 78,71	7,49 / 7,66	7,27 / 7,34	‡	80
Vc	$C_{26}H_{30}N_2O_2 \cdot H_2O$	74,17 / 74,26	7,39 / 7,67	6,58 / 6,66	‡	63
Vd	$C_{25}H_{27}N_3O_3 \cdot 1/2H_2O$	70,81 / 70,40	6,49 / 6,62	9,95 / 9,95	‡	78
Ve †	$C_{25}H_{27}N_3O_3 \cdot H_2O$	69,37 / 68,95	6,45 / 6,71	9,64 / 9,65	‡	51
VIIa	$C_{20}H_{26}N_2O \cdot 2H_2O$	69,50 / 69,33	8,68 / 8,73	7,95 / 8,09	133...135	87
VIIb †	$C_{25}H_{28}N_2O$	80,64 / 80,61	7,69 / 7,58	7,42 / 7,52	224...226	84
VIIe	$C_{25}H_{27}N_3O_3 \cdot 1/2H_2O$	70,32 / 70,40	6,86 / 6,62	9,35 / 9,85	209...211	68
VIIf	$C_{25}H_{27}N_3O_3 \cdot 1/2H_2O$	70,48 / 70,40	6,65 / 6,62	9,79 / 9,85	235...237	47
VIIg	$C_{27}H_{31}N_3O_3 \cdot 1/2H_2O$	71,44 / 71,34	6,94 / 7,10	9,19 / 9,24	221...223	79
VIIh	$C_{29}H_{36}N_2O \cdot 1/2H_2O$	79,81 / 79,59	8,43 / 8,52	6,22 / 6,40	145...147	76
VIIIa	$C_{21}H_{29}IN_2O \cdot 1/2H_2O$	54,76 / 54,67	6,68 / 6,55	5,76 / 6,07	248...249	88
VIIIb	$C_{26}H_{31}IN_2O \cdot 1/2H_2O$	59,54 / 59,66	6,04 / 6,16	5,17 / 5,23	155...157	45

*Drying at 120°C gave a water content of ~0.5 mole (from elemental analysis results)

†Sample dried at 120°C.

‡Do not have sharp melting points.

Compounds VII are very similar in structure to 1,2,3-trimethyl-2H-pyrrolo[3,4-*c*]quinoline, which has been described in the literature [6]. In both cases a bathochromic shift in the UV spectrum occurs on forming the salt, except for the *p*-nitrophenyl substituted compounds VIId, g in which there are hypsochromic shifts of the long-wavelength maximum with a broad shoulder to longer wave length, consequently the bathochromically shifted maxima are less intense.

2-Alkyl substituted pyrroloacridines VII are alkylated at position 6 on treatment with methyl iodide. The pyrroloacridinium iodides obtained (VIIIa, b) are more intensely colored than the starting materials VII and their UV spectra do not change on the addition of either acid or base.

TABLE 2. UV and IR Spectra of Derivatives of Pyrrolo[4,3,2-*m,n*]acridine II-VIII

Compound	Color of crystals	UV spectrum		IR spectrum, cm^{-1} (C=O)†
		medium*	λ_{max}, nm (lg ε)	
1	2	3	4	5
IIe	Yellow	Ethanol	210 (4,40), 226 (4,41), 318 (4,02), 430 (3,66)	1655‡
		Ethanol + HCl	207 (4,44), 265 (4,55), 316 (3,93), 444 (3,44)	
IIf	Yellow	Ethanol	202 (4,43), 236 (4,43), sh. 264 (4,15), sh 284 (3,80), 352 (4,23), 428 (3,68)	1655‡
		Ethanol + HCl	204 (4,58), 234 (4,43), 265 (4,43), 328 (4,26), 440 (3,50)	
IIIa	Red	Ethanol	202 (4,19), 238 (4,43), sh. 260 (4,10), 312 (3,44), 450 (3,60)	1682
IIIc	Red	Ethanol	202 (4,48), 264 (4,53), sh. 310 (3,82), 458 (3,41)	1685
IVa	Red	Ethanol	204 (4,36), 220 (4,41), 238 (4,37), 266 (4,04), 322 (3,46), 460 (3,41)	1693
		Ethanol + NH_4OH	206 (4,82), 221 (4,47), sh. 244 (4,27), sh. 280 (3,83), 346 (3,48), 490 (3,12)	
IVb	Red	Ethanol	204 (4,57), 215 (4,57), 264 (4,56), 324 (3,81), 456 (3,45)	1679
		Ethanol + NH_4OH	207 (5,01), sh. 220 (4,54), 282 (4,34), 354 (3,90), 500 (3,14)	
IVc	Reddish violet	Ethanol	204 (4,67), 216 (4,61), 267 (4,58), 326 (3,85), 464 (3,38)	1680
		Ethanol + NH_4OH	207 (5,02), 220 (4,63), 280 (4,42), 358 (3,93), 508 (3,24)	
IVd	Orange	Ethanol	206 (4,61), 218 (4,59), 255 (4,38), 386 (4,02), bend 438 (3,91)	1690
		Ethanol + NH_4OH	208 (5,13), sh. 222 (4,58), 258 (4,32), sh. 290 (4,14), 430 (4,18)	
IVe	Orange	Ethanol	210 (4,53), 264 (4,51), 318 (3,86), 440 (3,36)	1670
		Ethanol + NH_4OH	205 (4,77), 282 (4,34), 352 (3,92), plateau 410...530 (3,18)	
Vb**	Deep violet	Ethanol	204 (4,45), sh 228 (4,25), 266 (4,41), 332 (3,76), sh. 360 (3,48), 460 (3,26)	1678
		Ethanol + NH_4OH	206 (4,99), sh 233 (4,37), 282 (4,32), 354 (3,87), 504 (3,09)	
VIIa	Orange	Ethanol	202 (4,21), 243 (4,48), 440 (3,65)	1655‡
		Ethanol + HCl	202 (4,26), 238 (4,39), 266 (4,11), 311 (3,41), 454 (3,48)	
VIIb	Yellow	Ethanol	202 (4,25), 237 (4,19), 263 (4,08), 426 (3,49)	1657‡
		Ethanol + HCl	202 (4,36), 235 (4,13), 261 (4,25), 310 (3,41), 438 (3,35)	
VIId	Light orange	Ethanol	202 (4,44), 248 (4,47), 412 (4,01)	1677
		Ethanol + HCl	202 (4,50), 240 (4,39), 266, (4,36), 355 (3,78), sh 400...430 (3,59)	
VIIe	Yellow	Ethanol	205 (4,41), 237 (4,38), 266 (4,36), sh 310 (3,65), 418 (3,65)	1675
		Ethanol + HCl	204 (4,48), 234 (4,33), 265 (4,49), sh 306 (3,68), 432 (3,50)	

TABLE 2 (continued)

1	2	3	4	5
VIIg	Light orange	Ethanol	202 (4,42), 246 (4,42), sh. 286 (3,97), 412 (3,91)	1675
		Ethanol + HCl	202 (4,46), 239 (4,36), 267 (4,35), 350 (3,67), sh: 400...440 (3,54)	
VIIh	Yellow	Ethanol	203 (4,39), 238 (4,31), sh. 260 (4,16), 418 (3,55)	1670
		Ethanol + HCl	202 (4,42), 236 (4,21), 262 (4,30), sh. 308 (3,49), 436 (3,42)	
VIIIa	Red	Ethanol	204 (4,42), 219 (4,46), 240 (4,38), 274 (4,16), 322 (3,44), 456 (3,48)	1675
VIIIb	Light brown	Ethanol	202 (4,61), sh. 214 (4,53), 265 (4,38), 318 (3,53), 442 (3,44)	1683

*Parts of the spectra were recorded in ethanol containing ~0.15 mole/liter HCl (corresponding to spectra of the hydrochlorides) or NH_4OH.

†ν_{NH} of compounds IIf, g) 3420; hydrochloride IIIa) 3380 (NH) and 2800-2600 (N^+-H band); hydrochloride IIIc) 3340 (NH), 2750-2500 and 1850-1800 (N^+-H band). ν_{NH} for the pyrroloacridinium iodides was weak [IVa) 3420; IVc) 3400; IVe) 3340] or not resolved (IVb, IVd).

‡In chloroform.

**The crystals of betaines Va-c were deep violet and of Vd, e were violet red, but the UV spectra of ethanol solutions were similar to those of the iodides IV.

The ^1H NMR spectra (Table 3) confirm the structures of the synthesized derivatives of pyrroloacridine.

EXPERIMENTAL

IR spectra in Vaseline oil or chloroform solutions were recorded with a Perkin-Elmer 580B spectrometer, UV spectra with a Hitachi-557 spectrometer, and ^1H NMR spectra of DMSO-D_6 or $CDCl_3$ solutions with TMS as internal standard with a Bruker WH-90 spectrometer.

The xanthendiones I, the octahydropyrroloacridines II and their hydrochlorides III were synthesized by a known method [1]. The synthesis and characteristics of previously synthesized derivatives of pyrroloacridine are cited in the literature: compound IIa [5], compounds IIb-d and IIIb, d [1]. Only the UV spectra of hydrochlorides IIIe, f are cited in this paper (Table 2).

1-(3-Nitrophenyl)-4,4,8,8-tetramethyl-2,3,4,5,7,8,9,10-octahydropyrrolo[4,3,2-*m,n*]acridin-10-one (IIe). 9-(3-Nitrobenzoyl)-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8-octahydroxanthen-1,8-dione Ie (10.59 g, 0.025 mole), ethanol (50 ml) and 25% aqueous ammonia (30 ml, 0.44 mole) were heated in an autoclave at 140°C for 5 h to give yellow crystals of compound IIe (7.14 g), which were recrystallized from ethanol.

1-(4-Cyanophenyl)-4,4,8,8-tetramethyl-2,3,4,5,7,8,9,10-octahydropyrrolo[4,3,2-*m,n*]acridin-10-one (IIf) was synthesized analogously from the octahydroxanthendione (If).

Hydrochloride of 1,4,4,8,8-pentamethyl-2,3,4,5,7,8,9,10-octahydropyrrolo[4,3,2-*m,n*]acridin-10-one (IIIa) was obtained by adding conc. HCl (0.25 ml, 2.5 mmole) to a solution of pyrroloacridine IIa (0.82 g, 2.4 mmole) in hot ethanol (50 ml). After cooling, the red crystalline hydrochloride IIIa was obtained (0.77 g) and was recrystallized from ethanol.

Hydrochloride of 1-(4-Methoxyphenyl)-4,4,8,8-tetramethyl-2,3,4,5,7,8,9,10-octahydropyrrolo[4,3,2-*m,n*]acridin-10-one (IIIc) was prepared analogously with half as ethanol and the addition of ether to separate the product.

1-Methyl- and 1-Aryl-4,4,6,8,8-pentamethyl-10-oxo-2,3,4,5,7,8,9,10-octahydropyrrolo[4,3,2-*m,n*]acridinium Iodides (IVa-e). The corresponding pyrroloacridine (IIa-e) (3.0 mmole) was dissolved in methyl iodide (20 ml, 0.32 mole) and boiled for 2 h. In the case of the poorly soluble compounds, ethanol (8 ml) was added and the mixture heated for 5 h. The reaction mixture was evaporated in vacuum and the dried residue was recrystallized from ethanol. Ether was added to the solution in the case of compounds IVa and IVd.

TABLE 3. ^{1}H NMR Spectra of Derivatives of Pyrrolo[4,3,2-*m*,*n*]acridine II-VIII

Compound	Chemical shifts, δ, ppm, coupling constants (*J*), Hz						
	8-CH_3 and 4-CH_3 (two s, 2 × 6H)	9-CH_2 (s, 2H)	7-CH_2 and 5-CH_2 (two s, 2 × 2H)	3-CH_2 (s, 2H)	6-R^6	2-R^2	1-R^1
1	2	3	4	5	6	7	8
IIe *	1,12, 1,17	2,47	2,83 (s, 4H)	3,03	—	10,60 (1H, br. s, H)	7,40...8,15 (4H, m, $C_6H_4NO_2$)
IIf *	1,11, 1,16	2,50	2,83, 2,87	3,06	—	10,03 (1H, br. s, H)	7,25 (2H, d, *J* = 8,0, 2′,6′-H); 7,51 (2H, d, *J* = 8,0, 3′,6′-H)
IIIa	1,11, 1,14	2,55 †	3,03, 3,08	2,95	15,28 (1H, br. s, H)	13,58 (1H, br. s, H)	2,78 (3H, s, CH_3)
IIIc	1,11, 1,18	2,50†	3,10, 3,17	2,97	14,58 (1H, br. s, H)	13,72 (1H, br. s, H)	3,83 (3H, s, CH_3O); 6,94 (2H, d, *J* = 7,5, 3′,5′-H); 7,22 (2H, d, *J* = 7,5, 2′,6′-H)
IVa*	1,15, 1,22	2,60	3,08, 3,16	2,90	4,01 (3H, s, CH_3)	13,03 (1H, br. s, H)	2,87 (3H, s, CH_3)
IVb	1,13, 1,22	2,48 †	3,14, 3,30†	2,97	3,94 (3H, s, CH_3)	11,68 (1H, br. s, H)	7,10...7,41 (5H, m, C_6H_5)
IVc	1,05, 1,12	2,40†	3,05, 3,20†	2,90	3,83 (3H, s, CH_3)	11,77 (1H, br. s, H)	3,70 (3H, s, CH_3O); 6,84 (2H, d, *J* = 8,0, 2′,6′-H); 7,07 (2H, d, *J* = 8,0, 3′,5′-H)
IVd	1,13, 1,22	2,55†	3,15, 3,20	3,07	3,98 (3H, s, CH_3)	11,50 (1H, br. s, H)	7,49 (2H, d, *J* = 9,0, 2′,6′-H); 8,22 (2H, d, *J* = 9,0, 3′,5′-H)
IVe	1,14, 1,24	2,50†	3,19, 3,30†	3,05	3,98 (3H, s, CH_3)	11,50 (1H, br. s, H)	7,60...8,30 (4H, m, $C_6H_4NO_2$)
Va*	1,18, 1,19	2,51	2,84 (s, 4H)	2,75	3,68 (3H, s, CH_3)	—	2,89 (3H, s, CH_3)
Vb*	1,15 (s, 12H)	2,42	2,82 (s, 4H)	2,76	3,63 (3H, s, CH_3)	—	7,05...7,40 (5H, m, C_6H_5)

TABLE 3 (continued)

1	2	3	4	5	6	7	8
Vc*	1,16 (s, 12H)	2,44	2,85 (s, 4H)	2,78	3,68 (3H, s, CH_3)	–	3,80 (3H, s, CH_3O); 6,84 (2H, d, J = 9,0, 3',5'-H); 7,28 (2H, d, J = 9,0, 2',6'-H)
Vd*	1,20 (s, 12H)	2,52	2,91 (s, 4H)	2,82	3,75 (3H, s, CH_3)	–	7,45 (2H, d, J = 9,0, 2',6'-H); 8,15 (2H, d, J = 9,0, 3',5'-H)
Ve*	1,20 (s, 12H)	2,47	2,88, 2,90	2,81	3,73 (3H, s, CH_3)	–	7,31...8,15 (4H, m, $C_6H_4NO_2$)
VIIa*	1,15, 1,16	2,51	2,75, 2,80	3,02	–	3,69 (3H, s, CH_3)	2,91 (3H, s, CH_3)
VIIb*	1,07, 1,19	2,33	2,81 (s, 4H)	2,98	–	3,52 (3H, s, CH_3)	7,20...7,60 (5H, m, C_6H_5)
VIId*	1,04, 1,16	2,34	2,93, 2,97	2,80	–	3,65 (3H, s, CH_3)	7,46 (2H, d, J = 9,0, 2',6'-H); 8,20 (2H, d, J = 9,0, 3',5'-H)
VIIe*	1,07, 1,21	2,53	2,84, 2,85	3,01	–	3, 58 (3H, s, CH_3)	7,45...8,33 (4H, m, $C_6H_4NO_2$)
VIIf*	1,10, 1,22	2,36	2,83, 2,85	3,01	–	0,75 (3H, t, J = 7,0, γ-CH_3); 1,40...1,80 (2H, m, β-CH_2); 3,91 (2H, t, J = 7,5, α-CH_2)	7,38 (2H, d, J = 9,0, 2',6'-H); 8,25 (2H, d, J = 9,0, 3',5'-H)
VIIg*	1,06, 1,19	2,36	2,81, 2,84	3,00	–	0,73 (6H, d, J = 5,6, δ-CH_3); 1,30...1,50 (2H, m, β-CH_2); 3,20...3,70 (1H, m, γ-CH); 3,80...4,04 (2H, m, α-CH_2)	7,15...7,45 (5H, m, C_6H_5)
VIIIa*	1,22, 1,30	2,58	3,12, 3,40	2,98	4,10 (3H, s, CH_3)	3,82 (3H, s, CH_3)	2,82 (3H, s, CH_3)
VIIIb*	1,14, 1,34	2,39	3,09, 3,48	3,02	4,12 (3H, s, CH_3)	3,57 (3H, s, CH_3)	7,10...7,43 (5H, m, C_6H_5)

*In $CDCl_3$.

†Signal partially overlapped by the signal of the solvent.

1-Methyl- and 1-Aryl-4,4,6,8,8-pentamethyl-10-oxo-2,3,4,5,7,8,9,10-octahydroacridino[1,9*a*,9-*b*,*c*]-pyrrolates (Va-e). The corresponding pyrrolo[4,3,2-*m*,*n*]acridines IVa-e (2.0 mmole) were mixed with dichloromethane (30 ml) and 25% aqueous ammonia (10 ml, 0.15 mol). The mixture was stirred for 5 min and the aqueous layer removed. The violet solution of the corresponding compound Va-e in dichloromethane was washed twice with aqueous ammonia, then water, dried over anhydrous Na_2SO_4, and evaporated in vacuum. The dried residue was purified by dissolving dichloromethane and adding hexane.

2-Alkyl Derivatives of 1-Methyl- and 1-Aryl-4,4,8,8-tetramethyl-2,3,4,5,7,8,9,10-octahydropyrrolo[4,3,2-*m*,*n*]-acridin-10-ones (VIIa, b, d, e, g, h). Sufficient sodium hydride for quantitative formation of the anion (from 6 mmole for the unsolvated compound IIb to 16 mmole for the solvated compound IIa) was added to a solution of the corresponding pyrrolo[4,3,2-*m*,*n*]acridine IIa, b, d, e (5 mmole) in anhydrous hexamethylphosphoramide (30 ml) at room temperature. Rapid evolution of hydrogen occurred to give an intensely colored solution (dark red to deep blue, depending on the substituent R^1). When the reaction was completed (about 15 min) an alkyl halide was added in 10% excess based on the sodium hydride added. The reaction was complete in 15 min with methyl iodide at room temperature. With propyl iodide the reaction mixture was heated for 5 min and for isoamyl bromide for 15 min at 50°C. The reaction mixture was then stirred with 5% NH_4Cl solution (200 ml). A precipitate of the corresponding compound VIIa, b, d, e, g, and i formed over 1 h and was recrystallized from aqueous ethanol.

1,2,4,4,6,8,8-Heptamethyl-10-oxo-2,3,4,5,7,8,9,10-octahydropyrrolo[4,3,2-*m*,*n*]acridinium Iodide (VIIIa). A solution of compound VIIa (1.0 g, 2.92 mmole) in methyl iodide (20 ml, 0.32 mole) was boiled for 3 h, the excess methyl iodide was evaporated off, and the residue was dissolved in ethanol. Red crystalline compound VIIIa (0.95 g) was obtained after the addition of ether.

2,4,4,6,8,8-Hexamethyl-1-phenyl-10-oxo-2,3,4,5,7,8,9,10-octahydropyrrolo-[4,3,2-*m*,*n*]acridinium Iodide (VIIIb). A solution of compound VIIb (3.05 g, 8.19 mmole) in a mixture of methyl iodide (30 ml, 0.48 mole) and ethanol (10 ml) was boiled for 9 h. The reaction mixture was evaporated in vacuum. The dried residue was dissolved in dichloromethane (20 ml) and benzene (30 ml) was added. Orange crystals of compound VIIIb (1.9 g) were isolated.

The yields and characteristics of the compounds synthesized are given in Table 1, while their IR and UV spectra are given in Table 2 and their ^1H NMR spectra in Table 3.

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