flux condenser and immersed in a thermostat at the required temperature, was placed 12.5 mmole halide I or II, 105 mmole alkyl chloride, 15 ml chloroform, and the required quantity of catalyst and potassium carbonate, and the mixture was stirred for 3 or 5 h. The solid deposit was filtered off and washed with chloroform. The filtrate was evaporated in vacuum and the individual compounds isolated by chromatographing the residue on a column of silica gel with 6:6:1 chloroform–acetonitrile–water. The ratio of the reaction products was determined by liquid chromatography after removing resinous substances from the reaction mixture on a short column of silica gel. Salt VIII, $C_{22}H_{24}NBr$, mp 144-145°C. XI, $C_{29}H_{30}NBr$, mp 236-237°C.

B. To a mixture of 2.53 g (12.5 mmole) halide I, 12.1 ml (105 mmole) benzyl chloride, and 0.142 g (0.625 mmole) TEBA-Cl in a current of nitrogen was added 18 ml 25% NaOH. This was stirred (~1000 rpm) for 3 h in a thermostat at 45°C. The aqueous layer was extracted with chloroform, the extract combined with the organic layer and evaporated in vacuum. The residue was recrystallized from water. Yield 1.7 g compound XII, $C_{29}H_{30}NCl$, mp 205-206°C.

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REACTION OF ETHYL 9-THIOACRIDONYL-10-ACETATE WITH HYDRAZINE

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The reaction of ethyl 9-thioacridonyl-10-acetate with hydrazine hydrate gives the corresponding ethyl hydrazonoacridonyl-10-acetate, which readily undergoes a reaction with aldehydes and on heating in DMF reacts with hydrazine hydrate to form 9-ylidenehydrazonoacridonyl-10-acetic acid hydrazide. The latter undergoes a condensation reaction with aldehydes to form ylidenehydrazides of acridonyl-10-acetic acid 9-ylidenehydrazones. The structures of these compounds have been confirmed by UV, IR, PMR, and mass spectrometry.

Among acridine derivatives there are compounds which exhibit high antimicrobial [1], anti-inflammatory [2], and antitumor [3] activity.

With the aim of trying to find compounds with potential antimicrobial activity we have studied the reactivity of ethyl 9-thioacridonyl-10-acetate (I) towards hydrazine hydrate. It transpired that hydrazine attacks the $C_{(9)}$ atom and not the carbethoxy group:

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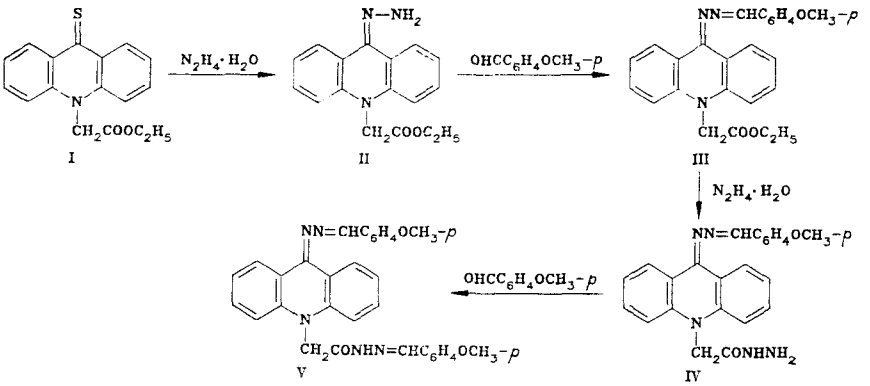

In the UV spectrum of compound II there are absorption bands at 232, 292, and 373 nm, which are characteristic of 9-acridone [4]. In the IR spectrum there are absorption bands due to an amino (3400 and 3350 cm^{-1}) and carbonyl group (1740 cm^{-1}).

In the mass spectrum (Table 1), a molecular ion peak (M^+) is recorded at 295.* The exact mass was recorded by high-resolution mass spectrometry (HRMS) – 295.1369 – which corresponds to the empirical formula $C_{17}H_{17}N_3O_2$. The ion peaks at 51, 76, 77, 102, 151, 152, 165, 166, 178, 179, 180 are typical for an acridine structure. The appearance of $[M - CH_3]^+$ (280), $[M - C_2H_4]^+$ (267), $[M - COOC_2H_5]^+$ (F, 222), and $[OC_2H_5]^+$ (45) indicate that there is an ester group as part of the molecule of II. The origin of the ions at 207 and 205 (see Table 1) was not clear. The HRMS data for these ions indicate an empirical formula $C_{13}H_9N_3$ ($[F - CH_3]^+$) and $C_{14}H_9N_2$ ($[F - NH_3]^+$) (found: 207.0829, calculated: 207.0797; found: 205.0752, calculated: 205.0768, respectively). Migration of a hydrogen atom, occurring on elimination of a CH_3 radical and an NH_3 molecule is only possible when there is spatial proximity of amine and N-methylenamine groups [5]. This order of decomposition was determined in the spectra of metastable ions using the technique DADI.

The proposed structure of compound II was also confirmed by the fact that its condensation with p-methoxybenzaldehyde on heating in ethanol in the presence of a catalytic quantity of sulfuric acid results in the formation of the corresponding ethyl 9-(p-methoxybenzylidene)hydrazonoacridonyl-10-acetate (III), which on heating for 1 h with hydrazine hydrate in DMF gives 9-ylidenehydrazonoacridonyl-10-acetic acid hydrazide (IV). Compound IV readily reacts with p-methoxybenzaldehyde to form 9-ylidenehydrazonoacridonyl-10-acetic acid ylidenehydrazide (V). The main method of identifying compounds III-V was mass spectrometry. In the mass spectrum of compound III an M^+ peak at 413 was detected (HRMS: found: 413.1783; $C_{25}H_{23}N_3O_3$; calculated: 413.1739). In the mass spectrum (Table 1) the signal corresponding to detachment of a $COOC_2H_5$ particle from M^+ is predominant (HRMS: found: 340.1464; $C_{22}H_{18}N_3O$; 340.1450). It is known that the azine bond usually does not break as a result of electron impact [6]. α-Cleavage of the bonds relative to the aryl (heterocyclic) rings is also a process that is energetically unfavorable, so the intensities of the ion peaks due to the azine part of the molecule of compound III are small: $[M - CH_3OC_6H_4]^+$ (306) (HRMS: found: 306.1264; $C_{18}H_{16}N_3O_2$; calculated: 306.1224) and $[CH_3O\text{-}p\text{-}C_6H_4\text{-}CH{=}N^+]$ (134) (HRMS: found: 134.0604; C_8H_8NO; calculated: 134.0606).

Similar patterns for the mass spectrometric fragmentation are shown by compounds IV and V (Table 1). The UV, IR, and PMR spectroscopic data are consistent with the proposed structures of compounds IV and V.

As a result of the conjugation between the acridone part of the molecule and p-methoxybenzaldehyde through the azine bridge, a new long-wavelength band appears at 418 nm in the UV spectrum. In the IR spectrum, vibrations due to ν_{NH_2} are absent.

EXPERIMENTAL

UV spectra were recorded on a Pye-Unicam spectrophotometer in quartz cells (d = 1.0 cm) in isopropanol solution; IR spectra were recorded on a Perkin–Elmer instrument in the form of KBr disks; PMR spectra were recorded on a Bruker WH-250 spectrophotometer in DMSO-d_6, with TMS as internal standard. Low- and high-resolution mass spectra and those of metastable ions

*The numbers characterizing the ions specify their m/z value.

TABLE 1. Mass Spectra of Compounds II-V

Compound	m/z value (I_{rel} of ion peaks, %) †
II	295 (95) M^+, 280 (10), 223 (19), 222 (100) F, 208 (21), 207 (45) $[F-CH_3]^+$, 206 (11), 205 (51) $[F-NH_3]^+$, 194 (17), 180 (21), 179 (15), 152 (11), 151 (10), 77 (10), 45 (10)
III	413 (36) M^+, 340 (56), 280 (21), 223 (17), 222 (100), 208 (21), 207 (40), 205 (15), 194 (17), 192 (10), 180 (24), 179 (16), 178 (10), 152 (13), 134 (10), 77 (15)
IV	399 (55) M^+, 384 (15), 340 (22), 223 (16), 222 (100) F, 207 (32), 205 (64), 194 (65), 192 (23), 180 (45), 179 (37), 178 (11), 165 (17), 152 (14), 151 (24), 135 (33), 134 (19), 77 (40), 76 (15), 59 (16), 51 (30)
V	517 (10), M^+, 384 (15), 340 (11), 277 (16), 223 (16), 222 (95), 207 (100), 205 (26), 194 (36), 192 (13), 180 (18), 179 (28), 177 (10), 152 (10), 149 (86), 135 (58), 134 (76), 77 (27), 76 (14), 51 (20)

*Temperature of admission system for compound II – 100°C, for compound III – 120°C; and for compound V – 260°C.
†Ion peaks with intensity ≥10% are given.

were recorded on an MAT-311A mass spectrometer under standard conditions. The elemental analysis data for C, H, and N corresponded to the calculated values.

Ethyl 9-Hydrazonoacridonyl-10-acetate (II, $C_{17}H_{17}N_3O_2$). Compound I (2.97 g, 0.01 mole) was dissolved in 100 ml of ethanol, 0.02 mole of hydrazine hydrate was added, and the mixture was heated on a water bath for 30 min until the evolution of H_2S had ceased. The reaction mixture was cooled and diluted with water. The precipitate was separated and dried. Yield 1.8 g (61%) of yellow needles with mp 141-143°C (from ethanol). UV spectrum (in ethanol), λ_{max} (log ε): 232 (4.74), 292 (3.90), 373 nm (3.94). IR spectrum: 3400 (ν_{NH_2}), 3350 (ν_{NH}), 3060 ($\nu_{CH_{Ar}}$), 2980-2930 (ν_{CH}), 1740 (ν_{CO}), 1603 (ν_{Ar}), 760 cm^{-1} ($\sigma_{CH_{Ar}}$). PMR spectrum: 1.26 (3H, t, CH_3, J = 6.5 Hz); 4.23 (2H, q, CH_2, J = 6.5 Hz); 4.55 (2H, s, CH_2); 6.47 (2H, br.s., NH_2); 6.90-8.17 ppm (8H, comp. m, protons of acridone ring).

Ethyl 9-(p-Methoxybenzylidene)hydrazonoacridonyl-10-acetate (III, $C_{25}H_{21}N_5O_2$). To a solution of 2.9 g (0.01 mole) of compound II in 100 ml of ethanol was added 1.36 g (0.01 mole) of p-methoxybenzaldehyde and 1 drop of H_2SO_4; the mixture was refluxed for 30 min until a yellowish precipitate had formed. The reaction mixture was cooled and the precipitate was separated and dried. Yield 3.7 g (90%) of red prisms with mp 184.5-186°C (from aqueous DMF, 1:1). UV spectrum, λ_{max} (log ε): 235 (4.60), 273 (4.20), 320 (4.0), 418 nm (3.78). IR spectrum: 3060, 3000-2890, 1740, 1640, 1603, 1260 ($ArOCH_3$), 880 (σ_{CH}, 1,4-substituted in benzene ring), 763 cm^{-1} (σ_{CH}). PMR spectrum: 1.27 (3H, t, CH_3, J = 6.5 Hz); 3.83 (3H, s, OCH_3): 4.24 (2H, q, CH_2, J = 6.5 Hz); 5.08 (2H, s, CH_2); 8.50 (4H, d.d, center of AB system, J = 8 Hz); 7.07-7.82 (8H, comp. m, protons of acridone ring), 8.54 ppm (1H, s, CH=N).

9-(p-Methoxybenzylidene)hydrazonoacridonyl-10-acetic Acid Hydrazide (IV, $C_{23}H_{21}N_5O_2$). To a solution of 4.13 g (0.01 mole) of compound III in 50 ml of DMF was added 0.02 mole of hydrazine hydrate, and the mixture was refluxed for 1 h, cooled, and diluted with water. The precipitate was separated and dried; yield 3.6 g (89%) of red flakes with mp 193-196°C (from ethanol). IR spectrum: 3380 (ν_{NH}), 3310 (ν_{NH_2}), 3080 ($\nu_{CH_{Ar}}$), 2960-2940 (ν_{CH}), 1670 (ν_{CO}), 1600 (ν_{Ar}), 750 cm^{-1} ($\sigma_{CH_{Ar}}$). PMR spectrum: 3.83 (2H, s, OCH_3), 4.85 (2H, s, CH_2), 7.49 (2H, br. d, NH_2), 7.00-7.85 (8H, comp. m, protons of acridone ring), 8.48 (4H, d.d, center of AB system, J = 2 Hz); 8.54 (1H, s, N=CH), 12.55 ppm (1H, br. t, NH).

9-(p-Methoxybenzylidene)hydrazonoacridonyl-10-acetic Acid p-Methoxybenzylidenehydrazide (V, $C_{31}H_{27}N_5O_3$). To a solution of 3.9 g (0.01 mole) of compound IV in 80 ml of ethanol was added 1.36 g (0.01 mole) of p-methoxybenzaldehyde and 1 drop of conc. H_2SO_4, and the mixture was heated for 20-30 min and cooled. The precipitate was separated and dried. Yield 3.6 g (93%) of red prisms with mp 174-175°C (from ethanol). PMR spectrum: 3.81 and 3.83 (3H and 3H, s, OCH_3); 5.10 (2H, s, CH_2); 7.05-7.80 (8H, comp. m, protons of acridone ring); 7.98 (4H, d. d) and 8.47 (4H, d. d, center of AB system, J = 9 Hz), 8.53 (1H, s, N=CH); 8.62 and 10.33 ppm (1H, br. s, NH).

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SYNTHESIS AND STRUCTURE OF N-SUBSTITUTED 2-AMINO-3-PHENACYLIDENE-3,4-DIHYDROQUINOXALINES

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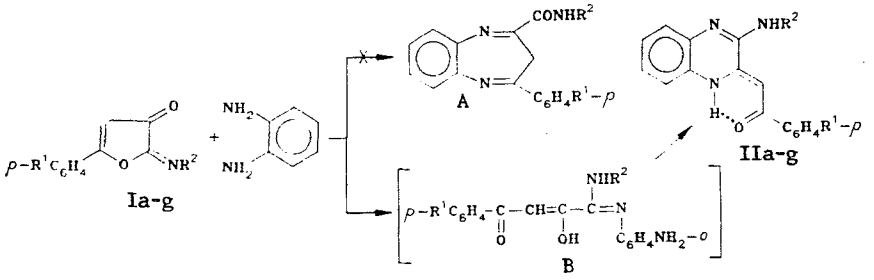
N-Substituted 2-imino-5-aryl-2,3-dihydro-3-furanones react with o-phenylenediamine to form N-substituted 2-amino-3-phenacylidene-3,4-dihydroquinoxalines.

It is known that N-substituted 2-imino-5-aryl-2,3-dihydro-3-furanones are readily decyclized by amines and water with nucleophilic attack occurring at $C_{(5)}$ of the heterocycle [1]. N-Substituted 2-imino-4,5-diaryl-2,3-dihydro-3-furanones [2] behave similarly with amines but hydrazines can attack both $C_{(5)}$ and $C_{(2)}$ [2].

With the aim of studying the chemical properties of N-substituted 2-imino-5-aryl-2,3-dihydro-3-furanones I we have investigated their reaction with o-phenylenediamine. The direction of nucleophilic attack at the $C_{(5)}$ atom or $C_{(2)}$ atom of compound I can lead to formation of either 1,4-benzodiazepine-2-carboxiamides A or to 2,3-disubstituted quinoxalines II, respectively.



I, II a–d $R^2=C(CH_3)_3$, a $R^1=H$, b $R^1=CH_3$, c $R^1=Br$, d $R^1=Cl$; e, f $R^2=p$-$CH_3C_6H_4SO_2CH_2$, e $R^1=H$, f $R^1=Cl$; g $R^2=2,5$-$(CH_3)_2C_6H_3$, $R^1=H$

We have shown that reaction of iminofuranones Ia-g with o-phenylenediamine at room temperature for 2-4 h gives the N-substituted 2-amino-3-phenacylidene-3,4-dihydroquinoxalines IIa-g. Evidently nucleophilic attack occurs only at atom $C_{(2)}$ of heterocycle I in this case with opening to the substituted amidines B and subsequent cyclization to the quinoxalines II.

The spectral characteristics of the compounds obtained confirmed their structure. The IR spectra of the alternative 1,4-benzodiazepin-2-carboxamides A show an "amide I" band near 1670 cm^{-1} [3] but this was absent in the spectra of IIa-g. The mass spectrum of IIc showed a molecular ion peak with m/z 399 and 397 together with fragment ion peaks at 384, 382 $[M - CH_3]^+$, 343, 341 $[M - C_4H_8]^+$, 185, 183 $[BrC_6H_4CO]^+$, and 158 $[M - C_4H_8 - BrC_6H_4CO]^+$.

Thanks to the presence of the amidine and aminovinylketone fragments the quinoxalines can exist in one of several tautomeric forms and a choice can be made based on their spectral data.

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