The remaining merocyanines were similarly obtained (Table 3).

The samples for the investigation of the photoconductivity were prepared by the following method. A 0.1-g sample of poly(butyl methacrylate) or polyorganosiloxane was dissolved in 1 ml of the solvent (toluene, benzene, or tetrahydrofuran), and the dye (1-5 wt.%) was added. The solution was filtered, the filtrate was poured over an aluminum support, and the support was dried in air and in a vacuum desiccator. Samples with a layer thickness of $3 \pm 0.5\ \mu$ were selected. For the determination of the photoinduced decrease in the potential in the near-UV region, the samples were irradiated with a DRSh-250 lamp through a UFS-1 light filter with $W = 10^{-5}$ Wt/cm^2. A 400-Wt incandescent lamp with a water filter with a thickness of 10 cm and $W = 10^{-4}$ Wt/cm^2 was used in the visible region as the source of photoexcitation.

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ACETALS OF LACTAMS AND ACID AMIDES

XX.* SYNTHESIS OF HYDROGENATED DERIVATIVES OF INDOLE, QUINOLINE, AND 1H,1-BENZAZEPINE

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Hydrogenated derivatives of indole, quinoline, and 1H,1-benzazepine were synthesized by reaction of 1-methyl-2-benzoylmethylenepyrrolidine, -piperidine, and -hexahydroazepine with acryloyl chloride. Alkylation of 1-methyl-5-oxo-8-benzoyl-1,2,3,4,5,6,7,8-octahydroquinoline with triethyloxonium tetrafluoroborate and subsequent treatment with sodium ethoxide gave the corresponding acetal, the reaction of which with substituted anilines gave 1-methyl-5-arylimino-8-benzoyl-1,2,3,4,5,6,7,8-octahydroquinolines. The IR and PMR spectra of the compounds are presented.

Enamino ketones I-III, which were obtained by condensation of lactam acetals with acetophenone [2], are promising substrates for the synthesis of condensed heterocyclic compounds that are of interest in the search for biologically active substances. The present paper is devoted to a study of the reaction of enamino ketones I-III with acryloyl chloride (IV). The synthesis of cyclohexene derivatives [3, 4] from noncyclic enamino carbonyl compounds and chloride IV and the reaction of 1-methyl-2-ethylidenepyrrolidine with acrolein, which

*See [1] for communication XIX.

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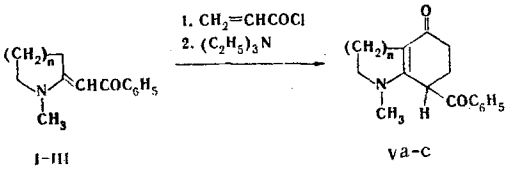
gives a tetrahydroindole derivative [5], served as prerequisites for the preparation of the two-ring compounds by this method.



I-III Va-c

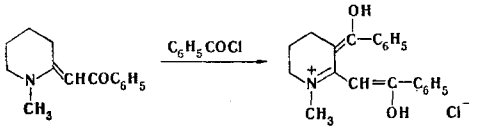
V a n=1; b n=2; c n=3

The reaction of 1-methyl-2-benzoylmethylenepyrrolidine (I), -piperidine (II), and -hexahydroazepine (III) with acryloyl chloride and subsequent treatment of the reaction mixture with triethylamine led to V, the IR spectra of which do not contain the absorption bands of OH groups nor bands characteristic for an unconjugated carbonyl group but do contain absorption bands at 1675 cm^{-1} related to the PhCO group and at 1600 and 1545 cm^{-1} (enamino ketone fragment). The PMR spectra of these substances (see the experimental section) contain a signal at 4.5-4.8 ppm related to the proton in the 7, 8, or 9 position (for Va-c) of the two-ring systems. The weak-field position of the observed signal is apparently due to the deshielding effect of the benzoyl group. Thus the set of spectral data indicates that compounds with structure V were synthesized in the reaction of acid chloride IV and enamino ketones I-III.

Proceeding from general considerations (see [3]) one can conclude that two-ring systems Va-c are formed either by O- or N-acylation of the starting enamino ketones and subsequent sigmatropic rearrangement (A) or by acylation at the C_3 atom and addition to the β position of the enamino ketone (B). However, we were unable to record the presence of intermediates by investigation of the reaction by polarography. Reduction waves of only the starting compounds and the final products were observed on the polarograms (see Table 1).

In this connection we carried out the benzoylation of enamino ketone II. The corresponding 3-benzoyl derivative (VI) was obtained in high yield; absorption bands of an OH group at 3340 cm^{-1} are observed in the IR spectrum of VI, but the band at 1730 cm^{-1} characteristic for an ester group is absent.

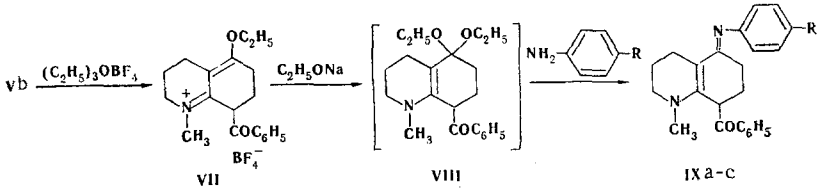
The PMR spectrum of this compound contains multiplets of signals of protons in the 4, 5, and 6 positions of the heteroring at 3.48, 1.84, and 3.79 ppm, respectively, and singlets of an $N-CH_3$ group at 3.55 ppm and of an α proton at 6.91 ppm.



II VI

In addition to an intense molecular ion peak (319), the mass spectrum of VI contains peaks that attest to the presence of a benzoyl group (214) in the VI molecule and correspond to elimination of the hydroxyl group of the molecular ion. This confirms the assumption that the second benzoyl group exists in the enol form.

However, it should be noted that in this case also one cannot exclude the possibility of initial reversible O- or N-acylation with a relatively slow shift of the equilibrium to favor the thermodynamically more favorable product VI due to irreversible benzoylation at $C_{(3)}$. Thus both pathway A and pathway B for the formation of two-ring systems V are extremely likely, and the realization of one or the other process (and, possibly, their simultaneous occurrence) is determined by the equilibrium constant of pathway A and the ratio of the rate constants of the reactions that occur.



VII VIII IX a-c

IX a R=CH3; b R=Cl; c R=OCH3

TABLE 1. Data from the Polarograms

Compound	$E_{1/2}$ (Ag)	$\varkappa = \frac{I_{lim}}{c}$
II	−1,56	2
	−2,05	2,43 (sum of two waves)
Vb	−1,46	1,15
	−2,26	2,4
Vb Hydrochloride	−0,75	0,54
	−1,25	0,33
	−1,48	0,39
	−2,27	1,2

In the case of Vb we attempted to activate its carbonyl group in the 5 position. The reaction of two-ring system Vb with triethyloxonium tetrafluoroborate proceeds smoothly (this is generally a characteristic of vinylogs of amides [6]), and tetrafluoroborate VII was obtained in high yield. The IR spectrum of VII contains absorption bands at 1680 (CO), 1610 ($C=\overset{+}{N}$), and 1580 (C = C) cm^{-1}, and the PMR spectrum is in complete agreement with structure VII (see the experimental section). However, tetrafluoroborate VII was found to be extremely inert with respect to nucleophilic reagents and could not be subjected to reaction with aromatic amines – in all cases starting VII was isolated. In this connection we synthesized the corresponding acetal (VIII), which was subjected, without isolation, to reaction with aromatic amines. 1-Methyl-5-arylamino-8-benzoyl-1,2,3,4,5,6,7,8-octahydroquinolines IXa-c were obtained by this method.

EXPERIMENTAL

The PMR spectra were recorded with a JNM-4H-100 spectrometer with tetramethylsilane as the internal standard. The IR spectra of mineral oil suspensionsof the compounds were recorded with a Perkin–Elmer 457 recording spectrometer. The mass spectra were obtained with an MKh-1303 spectrometer with direct introduction of the samples into the source. The ionizing-electron energy was 30 eV, and the temperature of the ionization chamber was 125°C. The polarograms were recorded in a polarographic cell thermostatted at 25 ± 0.1°C in a PO-4 polarograph (Radiometer, Denmark). The characteristics of the dropping mercury electrodes were as follows: 0.3 sec, m 0.73 mg/sec. The anode was a silver wire submerged in the solution to be polarographed. Samples of the reaction mixture (0.2 ml) were diluted to 5 ml with DMF; 0.5 ml of this solution was placed in the cell containing 2 ml of 0.1 M $(C_4H_9)_4NClO_4$ solution in DMF, and the polarogram was recorded after removal of the oxygen with a stream of nitrogen.

1-Methyl-5-oxo-8-benzoyl-1,2,3,4,5,6,7,8-octahydroquinoline (Vb). A solution of 1.95 ml (0.02 mole) of acryloyl chloride in 60 ml of dry benzene was added dropwise with refluxing in the course of 5.5 h to a solution of 4.3 g (0.02 mole) of II in 200 ml of dry benzene, after which 8 ml of triethylamine was added, and the mixture was refluxed for another 30 min. The cooled solution was decanted, the filtrate was evaporated, and the residue was triturated with ethyl acetate to give 2 g of Vb with mp 220-221°C.

The residue after decantation of the benzene solution was dissolved in chloroform, water and 5 ml of triethyl amine were added (to pH 9), and the aqueous layer was separated and extracted with chloroform. The combined extracts were dried with Na_2SO_4 and filtered, and the filtrate was evaporated. The residue was triturated with ethyl acetate to give another 2.3 g of Vb with mp 220-221°C. The overall yield of Vb, with mp 223-224°C (from isopropyl alcohol), was 4.3 g (80%). Mass spectrum: M^+ 269. IR spectrum: 1675 (COC_6H_5), 1600, 1580 cm^{-1} (enamino ketone). UV spectrum: λ_{max} 316 nm (log ε 4.45). PMR spectrum (in $CHCl_3$): 1.85 (3-CH_2), 2.26-2.45 (4,6,7-CH_2), 2.80 (N–CH_3), 3.20 (2-CH_2), 4.64 (8-CH), 7.47-8.05 (C_6H_5) ppm. Found: C 76.0; H 7.0%. $C_{17}H_{19}NO_2$. Calculated: C 75.8; H 7.1%. The hydrochloride of Vb had mp 196-197°C [from acetone–alcohol (2:1)]. PMR spectrum (in DMSO): 1.85 (3-CH_2), 2.30 (4,6,7-CH_2), 3.24 (N–CH_3), 3.64 (2-CH_2), 5.63 (C–H), 7.50-8.21 (C_6H_5) ppm. Found: Cl 11.5%. $C_{17}H_{19}NO_2 \cdot HCl$. Calculated: Cl 11.9%.

1-Methyl-6-oxo-9-benzoyl-1H,2,3,4,5,6,7,8,9-octahydrobenz[2,3-b]azepine (Vc). A solution of 1.5 ml (0.015 mole) of acryloyl chloride in 45 ml of dry benzene was added with refluxing in the course of 4.5 h to a solution of 3.5 g (0.015 mole) of 1-methyl-2-benzoylmethylene-1H,2,3,4,5,6,7-hexahydroazepine (III) in 150 ml of dry benzene, after which 12 ml of triethylamine was added, and the mixture was refluxed for another 30 min. The cooled solution was filtered, and the filtrate was evaporated. The residual oil was triturated in acetone, and the mixture was filtered through a layer of silica gel. The adsorbent was washed with 300 ml of acetone,

the acetone solution was evaporated, and the residue was triturated with ether to give 1.6 g (38%) of Vc with mp 156-157°C (from isopropyl alcohol). Mass spectrum: M^+ 283. IR spectrum: 1675 (COC_6H_5), 1605, 1545 cm^{-1} (enamino ketone). UV spectrum: λ_{max} 323 nm (log ε 4.40). PMR spectrum (in $CHCl_3$): 1.79 (3,4-CH_2), 2.16 (5,7-CH_2), 2.58 (8-CH_2), 2.77 (N−CH_3), 3.15-3.65 (2-CH_2), 4.77 (9-CH), 7.40-8.05 (C_6H_5) ppm. Found: C 76.0; H 7.5%. $C_{18}H_{21}NO_2$. Calculated: C 76.3; H 7.4%.

1-Methyl-4-oxo-7-benzoyl-2,3,4,5,6,7-hexahydroindole (Va). A solution of 2.0 ml (0.02 mole) of acryloyl chloride in 60 ml of dry benzene was added with refluxing to a solution of 4.0 g (0.02 mole) of enamine I in 200 ml of dry benzene in the course of 4.5 h, after which 8 ml of triethylamine was added, and the mixture was refluxed for another 30 min. Workup as in the case of Vc gave 1.1 g (20%) of Va with mp 208-209°C (from ethyl acetate). Mass spectrum: M^+ 255. IR spectrum: 1676 (COC_6H_5), 1605, 1565 cm^{-1} (enamino ketone). UV spectrum: λ_{max} 324 nm (log ε 4.39). PMR spectrum (in $CHCl_3$): 2.33 (3,5-CH_2), 2.76 (N−CH_3), 2.90 (6-CH_2), 3.63 (2-CH_2), 4.52 (7-CH), 7.60-8.10 (C_6H_5) ppm. Found: C 75.0; H 6.8; N 5.3%. $C_{16}H_{17}NO_2$. Calculated: C 75.3; H 6.7; N 5.5%.

1-Methyl-2-benzoylmethylene-3-benzoylpiperidine Hydrochloride (VI). A solution of 1.25 ml (0.01 mole) of benzoyl chloride in 15 ml of dry benzene was added at 20°C in the course of 4 h to a solution of 2.1 g (0.01 mole) of enamine II in 50 ml of dry benzene, and the resulting precipitate was removed by filtration to give 2.7 g (30%) of VI with mp 275-276°C (from isopropyl alcohol). Mass spectrum: M^+ 319. IR spectrum: 1575, 1595 (C = C), 1630 (C = $\overset{+}{N}$), 3340 (OH) cm^{-1}. PMR spectrum (in DMSO): 1.84 (5-CH_2), 3.48 (6-CH_2), 3.55 (N−CH_3), 3.79 (4-CH_2), 6.91 (α-CH)/7.40−8.14 (C_6H_5) ppm. Found: C 69.2; H 7.2; Cl 8.5%. $C_{21}H_{21}NO_2$. HCl. i-C_3H_7OH. Calculated: C 69.3; H 7.2; Cl 8.5%.

1-Methyl-5-ethoxy-8-benzoyl-1H,2,3,4,6,7,8-hexahydroquinoline Tetrafluoroborate (VII). A solution of 7.7 g (0.04 mole) of triethyloxonium tetrafluoroborate in 50 ml of dry methylene chloride was added in the course of 1 h to a suspension of 10.9 g (0.04 mole) of Vb in 100 ml of dry methylene chloride, after which the solvent was evaporated, and the residue was triturated in dry ether to give 15.1 g (97.5%) of VII with mp 140-141°C (from isopropyl alcohol). IR spectrum: 1580, 1610 (C = C, C = $\overset{+}{N}$), 1680 cm^{-1} (COC_6H_5). PMR spectrum (in DMSO): 1.34 (5-CH_3), 1.89 (3-CH_2), 2.33 (4,6,7-CH_2), 3.26 (N−CH_3), 3.71 (2-CH_2), 4.29 (O−CH_2), 5.41 (C−H), 7.50-8.14 ppm (C_6H_5). Found: C 59.4; H 6.4; N 3.5%. $C_{19}H_{24}BF_4NO_2$. Calculated: C 59.2; H 6.2; N 3.6%.

1-Methyl-5-(p-tolylimino)- 8-benzoyl-1,2,3,4,5,6,7,8-octahydroquinoline (IXa). A 10.6-g sample of fluoroborate complex VII was added at 2°C to solution of 0.69 g (0.03 g-atom) of sodium in 100 ml of absolute alcohol, and the mixture was allowed to stand at 2 h. The precipitate was removed by filtration, washed with water, and converted to 1.3 g of starting Vb. The filtrate was evaporated, and the residue was triturated with absolute ether. The mixture was filtered, and the ether solution was evaporated to give 4.6 g of acetal VIII. A solution of 4.6 g (0.014 mole) of acetal VIII and 1.47 g (0.014 mole) of p-toluidine in 80 ml of dry toluene was refluxed for 4 h, after which it was evaporated, and the residue was triturated with hexane. The mixture was filtered to give 2.6 g (30%) of amine IXa with mp 163-164°C (from isopropyl alcohol). IR spectrum: 1685 (CO), 1550, 1590 cm^{-1} (C = C, C = N). Found: C 80.5; H 7.2; N 7.7%. $C_{24}H_{26}N_2O$. Calculated: C 80.5; H 7.3; N 7.8%; A similar procedure was used to obtain IXb, with mp 171-172°C (from isopropyl alcohol), in 35% yield. IR spectrum: 1685 (CO), 1545, 1595 cm^{-1} (C = C, C = N). Found: C 72.9; H 6.3; Cl 9.2; N 7.7%. $C_{23}H_{23}ClN_2O$. Calculated: C 72.9; H 6.1; Cl 9.4; N 7.4%; This procedure was also used to obtain IXc, with mp 213-214°C (from isopropyl alcohol), in 36% yield. IR spectrum: 1685 (CO) 1550, 1590, 1600 cm^{-1} (C = C, C = N). Found: C 76.9; H 6.5; N 7.3%. $C_{24}H_{26}N_2O_2$. Calculated: C 77.0; H 7.0; N 7.5%.

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