Kinetics of the Reaction of the Phenazyl Radicals with Carbazole. Equal volumes of solutions of dihydrophenazine Ia-d (10^{-3} M) and carbazole (10^{-2} M) in benzene and powdered lead dioxide were placed in separate compartments of a cuvette. After evacuation and generation of the radical, its solution was mixed with the carbazole solution, the mixture was stirred rapidly, and the ESR signal was recorded at 20-50° as in the case of the recombination process.

Preparation of III. A 20-g sample of lead dioxide was added to 2 g (4.5 mmole) of dihydrophenazine Ia in 4.5 liters of dry benzene, and the mixture was stirred at room temperature for 1.5 h, after which 1.1 g (9 mmole) of freshly distilled monoethylaniline was added to a thoroughly filtered (to remove the oxidizing agent) solution of the radical, and the solution was stirred for 30 min. It was then chromatographed with a column filled with Al_2O_3. The eluate of the first zone contained 1.3 g of dihydrophenazine Ie, and the eluate of the second zone contained 0.5 g of III. Recrystallization of III from acetone gave violet crystals with mp 276° in 20% yield. Found: N 17.9%. $C_{26}H_{19}N_7O_8$. Calculated: N 17.6%.

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SYNTHESIS AND NITRATION OF 4-PHENYL-2,3-DIHYDRO-1H-1,5-BENZODIAZEPIN-2-ONE

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Analysis of the UV spectra of the reaction products shows that in the nitration of 4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one the nitro group is directed to the benzodiazepine ring rather than to the phenyl ring to give a 7-nitro derivative.

It has been shown that the nitration of 4-methyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one leads to the formation of a 7-nitro derivative [1], i.e., substitution takes place in the para position relative to the amide group rather than para to the ketimine group. The introduction of a phenyl group in the 4 position could, in view of the conjugation of the π electrons of the substituent with the carbon–nitrogen double bond [2], create, on the one hand, conditions for coplanarity of the rings and, on the other, substantially raise the electron density on the $C_{(3)}$ atom. In addition, if protonation proceeds precisely at this double bond, incorporation of a nitro group in the benzene ring of the subsituent would be likely.

It was found that nitration of 4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (I) by the action of potassium nitrate in concentrated sulfuric acid gives nononitro compound II, the acid hydrolysis of which leads to 4-nitro-o-phenylenediamine, indicating that the nitro group is attached to $C_{(7)}$ or $C_{(8)}$ of the diazepine portion of the molecule. The considerable yield of II and the absence in the reaction mixture of other substances are probably associated with protonation at the N_5 atom, as a result of which coordinated orientation of the protonated nitrogen atom and the acetamido group is observed [3]. The structure of this substance as precisely the 7 isomer was confirmed by alternative synthesis from N-(2,4-dinitrophenyl)benzoylacetamide (IV), the reductive

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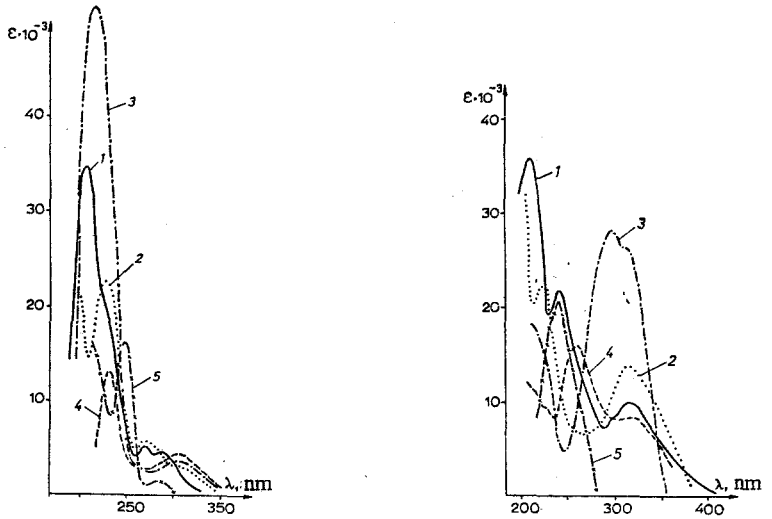
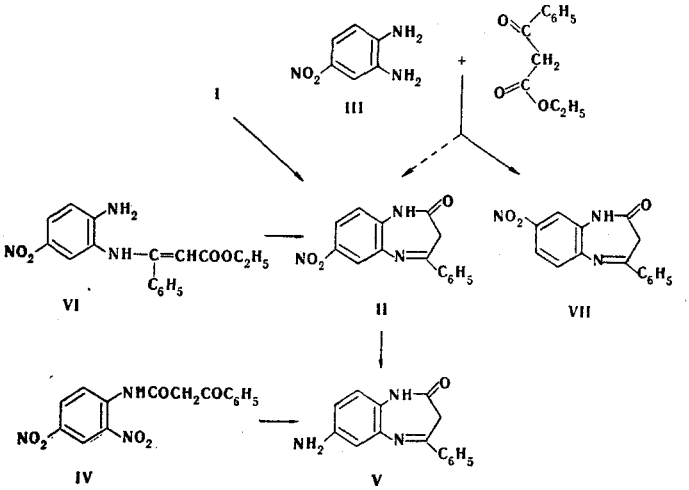


Fig. 1. UV spectra of 4-methyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (1, 2), 1H-2,3,4,5-tetrahydro-1,5-benzodiazepin-2-one (3, 4), and styrene (5): 1), 3), and 5) in alcohol; 2) and 4) in 1 N HCl.

Fig. 2. UV spectra of I (1, 2), stilbene (3), benzylideneaniline (4), and benzylidenemethylamine (5): 1), 3), 4), and 5) in alcohol; 2) in 1 N HCl.

cyclization of which led to 7-amino-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (V), which was identical to the product of reduction of diazepine II. In addition, benzodiazepinone II was synthesized by cyclization of ethyl 3-(4-nitro-2-aminophenylamino)cinnamate (VI) in the presence of sodium ethoxide.



However, the physical constants of the compound obtained were not in agreement with those previously published [4]. Hideg and Hankovsky [4] adopted a structure without proof, whereas the reaction of diamine III with benzoylacetic ester was carried out under severe conditions, for which isomerization is fully likely. We reproducted their experiment, obtained a substance with the constants described by them, and showed that it has 8-isomer structure VII.

In this connection, we made a systematic study of the electronic spectra of a number of 1,5-benzodiazepin-2-ones. The origin of the spectra was investigated by analysis of the structure into the component cochromophore systems by the method in [5].

The existence of noncoplanarity and the appearance of bands of two quasi-autonomous systems – the K_a band for the first case and the K band for the second – can be predicted in the spectrum of 4-methyl-1,5-benzodiazepin-2-one (VIII) with allowance for the possibility of conjugation of the double of the nitrogen atom

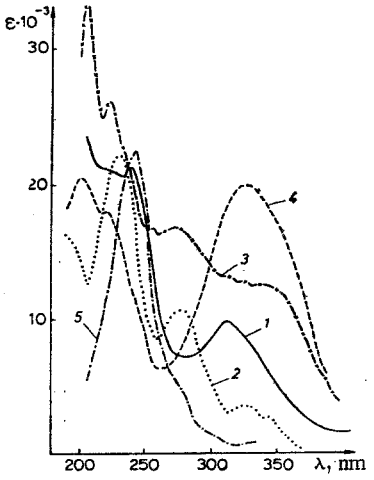


Fig. 3

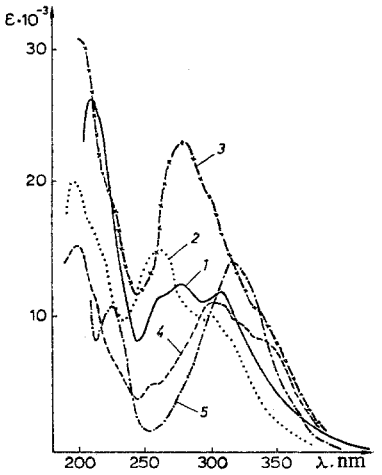


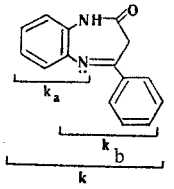
Fig. 4

Fig. 3. UV spectra of IX (1, 2), VII (3, 4), and m-nitroacetanilide (5): 1), 3), and 5) in alcohol; 2) and 4) in 50% sulfuric acid.

Fig. 4. UV spectra of X (1, 2), II (3, 4), and p-nitroacetanilide (5): 1), 3), and 5) in alcohol; 2), and 4) in 50% sulfuric acid.

and the CH = N group with the electrons of the benzene ring. On the basis of a comparison of the spectra of VIII with the spectrum of 1, 5-tetrahydrobenzodiazepinone [6], in which conjugation of the amino group with the benzene ring is realized, and the spectrum of styrene, in which the double bond is in conjugation with the ring λ_{max} at 211 nm (ε = 34,000) should be assigned to the K_a band. The hypsochromic shift ($\Delta\lambda$+10 nm) is apparently connected with replacement of the $NHCH_2$ group by $-N=CH-$, and the decrease in intensity ($\Delta\varepsilon$ = 8000) is explained by competitive conjugation of the double bond with the electrons of the benzene ring. The presence in the spectrum of a small inflection ($\lambda \sim 230$ nm), which is located close to the band of styrene (λ_{max} 248 nm), can be assumed to be a manifestation of the K system. The assignment of the bands is confirmed by a study of the spectrum of VIII in an acidic medium, in which protonation of the N_5 atom is likely. The absence of absorption in the region of the first intense maximum characteristic for the tetrahydrodiazepine system provides evidence in favor of the correct assignment of this band, and the increase in the intensity of the second band is evidently associated with the increase in the coplanarity of a system of the styrene type, as well as with the superimposition of the band of a protonated K_a system (Fig. 1).

When a phenyl ring is introduced in the 4 position, bands of three quasi-autonomous systems appear in the spectrum: the band at λ_{max} 310 nm, which is close to the band of stilbene (Fig. 2), can be assigned to the band of a unified conjugated system, the intense band at λ_{max} 240 nm can be assigned to a K_b system because of its similarity to the $C_6H_5CH=N-CH_3$ band (λ_{max} 246 nm), and the third band at λ_{max} 212 nm can be assigned to the aniline system of the molecule.



I

An increase in intensity is observed as a result of protonation, and this constitutes evidence for a change in the planar character of the molecule and probably is associated with an increase in the coplanarity of the system.

The introduction of a nitro group leads to considerable changes in the spectra (Fig. 3 and 4), in which additional absorption bands characteristic for nitroanilines and nitroacetamides appear. The bands of nitroacetamides, which are retained in the case of protonation, are the most characteristic bands. The λ_{max} bands at 242 nm for 8-nitro-4-methyl-1H-2,3-dihydro-1,5-benzodiazepin-2-one (IX) and 226 nm for VII, which undergo

considerable changes when the molecules are protonated, can be assigned to the absorption of the m-nitroacetanilide grouping, while the band at 310-320 nm is more characteristic for II and 7-nitro-4-methyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (X).

Thus the position of the nitro group can be determined on the basis of the UV spectra of nitrodiazepinones in acidic media from the appearance of a m-nitroacetanilide band in the spectra.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra of alcohol and sulfuric acid–water (1:1) solutions of the compounds were recorded with an SF-16 spectrophotometer. The PMR spectra of chloroform solutions were recorded with a Varian T-60 spectrometer with tetramethylsilane as the internal standard. The individuality of the compounds was monitored by means of thin-layer chromatography (TLC) on aluminum oxide in a chloroform–alcohol system (20:1).

Ethyl 3-(2-Aminophenylamino)cinnamate. This compound, with mp 133-135° (from ether–hexane), was obtained in 72% yield from o-phenylenediamine and benzoylacetic ester in the presence of catalytic amounts of acid. Found: N 10.1%. $C_{17}H_{18}N_2O_2$. Calculated: N 9.9%. PMR spectrum: 1.30 (t, CH_3), 4.13 (q, CH_2), 5.00 (s, 2H), and 3.63 ppm (s, NH_2).

4-Phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (I). This compound, with mp 205° (from alcohol), was synthesized in 65% yield from ethyl 3-(2-aminophenylamino)cinnamate by the method in [7]. Found: N 11.9%. $C_{15}H_{12}N_2O_2$. Calculated: N 11.9%. No melting-point depression was observed for a mixture of this product with the substance obtained by the method in [4], and their IR spectra were identical.

Ethyl 3-(2-Amino-5-nitrophenylamino)cinnamate (VI). Two to three drops of concentrated hydrochloric acid were added to a mixture of 3.06 g (0.02 mole) of 4-nitro-o-phenylenediamine in 14.5 ml (0.1 mole) of benzoylacetic ester, and the mixture was allowed to stand for 15 days. The resulting precipitate was washed with methanol and crystallized from benzene to give 2.9 g (45%) of a product with mp 203° (from benzene). Found: N 12.6%. $C_{17}H_{17}N_3O_4$. Calculated: N12.8%. PMR spectrum: 1.1 (t, CH_3), 4.28 (q, CH_2), and 5.29 ppm (s, CH).

7-Nitro-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (II). A) A 2.3-g (0.01 mole) sample of I was dissolved in 10 ml of concentrated sulfuric acid, the solution was cooled to -15°, and a solution of 1.01 g (0.01 mole) of potassium nitrate in 7 ml of concentrated sulfuric acid was added dropwise. The mixture was stirred at–10 to +6° for 2 h, after which it was poured into cold water, and the precipitate was removed by filtration to give 2 g (71%) of a product with mp 254° [from dimethylformamide (DMF)].

B) A 0.98-g (0.003 mole) sample of ester VI was refluxed with sodium ethoxide (from 0.22 g of sodium and 8.5 ml of alcohol) for 1 h, after which the solvent was removed, the residue was diluted with 10 ml of water, and the mixture was neutralized to p H 6. The resulting precipitate was removed by filtration and crystallized from DMF. No melting-point depression was observed for a mixture of this product with the substance obtained in method A, and their IR and UV spectra were identical. Found: C 63.5; H 4.5%. $C_{15}H_{11}N_3O_3$. Calculated: C 63.6; H 4.6%.

N-(2,4-Dinitrophenyl)benzoylacetamide (IV). A solution of 6 g (0.033 mole) of 2,4-dinitroaniline in xylene was added dropwise in the course of 24 h, with simultaneous removal of xylene by distillation, to a refluxing solution of 20 ml (0.14 mole) of benzoylacetic ester in 40 ml of xylene at 145-150°. The mixture was then cooled, and the precipitate was removed by filtration and washed with acetone to give 3.4 g (32%) of a product with mp 165° (from chloroform). Found: C 54.8; H 4.1%. $C_{15}H_{11}N_3O_6$. Calculated: C 54.7; H 3.3%.

7-Amino-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (V). A) A solution of 0.56 g (0.002 mole) of IIa in 25 ml of absolute alcohol was hydrogenated over Raney nickel. After the calculated amount of hydrogen had been absorbed, the catalyst was removed by filtration, and the solvent was removed from the filtrate to give 0.35 g (70%) of a product with mp 217° (from alcohol). Found: C 71.5; H 5.8%. $C_{15}H_{13}N_3O$. Calculated: C 71.7; H 5.1%.

B) A 1.6-g (0.005 mole) sample of IV was similarly hydrogenated. The ethanol was removed, and the residue was separated on aluminum oxide (elution with chloroform) to give 0.45 g (34%) of a product with mp 217°. The IR and UV spectra of the product and the compound obtained in experiment A were identical.

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MASS SPECTRA OF TRISUBSTITUTED 1,2,3,4-TETRAHYDRO-1,5-BENZODIAZOCIN-2-ONES

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The mass spectra of 1,5-benzodiazocin-2-ones are characterized by multiline character due to the large number of pathways of fragmentation of the molecular ions. In a number of cases the same signal in the high m/e region corresponds to ions with different compositions. The principal fragmentation pathways were determined by high-resolution mass spectrometry. The possible structures of the fragment ions and the mechanisms of their formation are discussed. The mass spectra of model compounds were also investigated for this purpose.

In order to compare the mass spectrometric behavior of benzodiazepinones [1, 2] with their eight-membered analogs we studied the mass spectra of a series of trisubstituted 1,2,3,4-tetrahydro-1,5-benzodiazocin-2-ones (Table 1). The compounds were synthesized under conditions close to those described in [3]. Their structures were proved by IR and UV spectroscopy and polarography. Thus absorption bands of C = O (1670 cm^{-1}) and C = N (1615 cm^{-1}) bonds are observed in the IR spectrum of II (solution in CCl_4). The UV spectrum of this compound in ethanol is characterized by absorption at 249 nm. Like the corresponding 1h-2,3-dihydro-1,4-benzodiazepin-2-ones [4], these compounds are reduced on a dropping mercury electrode and give one polarographic wave at 950-1020 mV, which evidently corresponds to reduction of the $N_5 = C_6$ bond.

The mass spectra of the investigated compounds and the calculated stabilities with respect to electron impact (W_M) are given in Table 2, and the ratios of the intensities of some of the characteristic ions are given in Table 3.

The W_M values demonstrate that the stabilities of the benzodiazocine molecules with respect to electron impact are lower by a factor of 2-2.5 than the stabilities of benzodiazepinones [2]; this is apparently due to the increase in the number of possible fragmentation pathways. It is interesting to note that the stabilities of N-alkyl-1,5-benzodiazocine molecules with respect to electron impact approach the stabilities of 3-alkyl-substituted benzodiazepinones [2].

The $[M - H]^+$ ion peaks have higher intensities, and in all cases their intensities exceed the intensities of the molecular ion peaks (with a correction for the monoisotope effect). The J_{M-1}/M ratios for I-XI range from 1.02 to 1.87, whereas J_{M-1}/J_M is 3.56 for I (R^1 = H). The J_{M-28}/J_M value for this compound also differs substantially. Whereas it is 0.79-1.57 for the entire series of compounds, it is 3.05 for I.

The mass spectra of I obtained with an MKh-1303 spectrometer are presented in Fig. 1, and the high-

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