of potassium carbonate and extracted with ether. The ether was removed by evaporation, and the residue was chromatographed with a column filled with Al_2O_3.

Compounds IIb-g were similarly obtained (see Table 2).

5,7-Dimethylbenzo[c]-α-carboline (IIf). A 0.09-g (3 mmole) sample of If was refluxed for 4 h with 2 ml of phosphorus oxychloride, after which the excess phosphorus oxychloride was removed by distillation, and the residue was treated with 10% aqueous potassium carbonate solution and extracted with ether. The ether was evaporated, and 0.025 g (34%) of IIf was isolated preparatively in a thick layer of Al_2O_3 [benzene–methanol (35 : 1)]. PMR spectrum, δ, ppm: 3.15 (s, 3H, 5-CH_3), 3.93 (s, 3H, 7-CH_3), and 7.48 (m, 8H, aromatic). The mass spectrum contained an $M^{+\cdot}$ peak at 246 (calculated value 246).

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3-(INDOLYLAMINO)VINYL KETONES

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The reaction of 5- and 6-aminoindoles with 1,3-diketones leads to 3-(indolylamino)vinyl ketones, which have an enamino ketone structure. A study of the mass-spectral fragmentation of the enamino ketones makes it possible to unambiguously determine the direction of the reaction and also to distinguish and identify isomeric pairs.

Aromatic amines react with 1,3-dicarbonyl compounds to give 3-(arylamino)vinyl ketones (arylamino crotonates in the case of acetoacetic ester) [1], which, for a series of models, are converted to the corresponding ketimines. The ketimine form was even found to be the preferred form in the case of the products of condensation of p-phenylenediamines having an electron-acceptor group in the ring with acetoacetic ester [2]. The solution of the problem of the structure of substances of this sort in solution frequently requires a precise study of the PMR spectra (for example, see [1]), and in the case of the solid state this can be accomplished by means of the mass spectra [3]. In a number of heteroaromatic amines the problem is complicated by the fact that for electron-surplus compounds (for example, for 2-aminoindoles [4]) condensation with 1,3-dicarbonyl compounds generally may occur with primary attack on the adjacent carbon atom rather than on the amino group, and, consequently, the necessary compounds generally are not formed in this reaction. Moreover, the overall reactivities of heteroaromatic amines depend substantially on the position of the amino group in the aromatic ring. They cannot always be predicted, since, for example, for indoles, transmission of the effect of substituents through the aromatic systems is not subject to simple principles [5].

In connection with the above, we made a study of the reaction of 5- and 6-aminoindoles (Ia and Ib) with 1,3-diketones.

As in the condensation with aniline [6], the reaction with acetylacetone proceeds considerably more readily than in the case of dibenzoylmethane, the electrophilicity of the carbonyl atoms of which is considerably lower. The PMR spectra of IIa-f [in dimethyl sulfoxide (DMSO)–acetone] contain signals of protons of vinyl and imino

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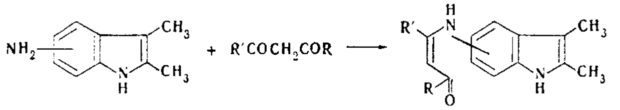
groups, and this constitutes evidence in favor of an enamino ketone structure. When the starting ketone contains a phenyl group, these signals are shifted to weak field (by up to 1 ppm); this can be explained by the effect of the ring current of the phenyl ring. As usual in the case of conjugated enamino ketones [1], a broad band at 1600-1620 cm^{-1} is observed in the IR spectra.

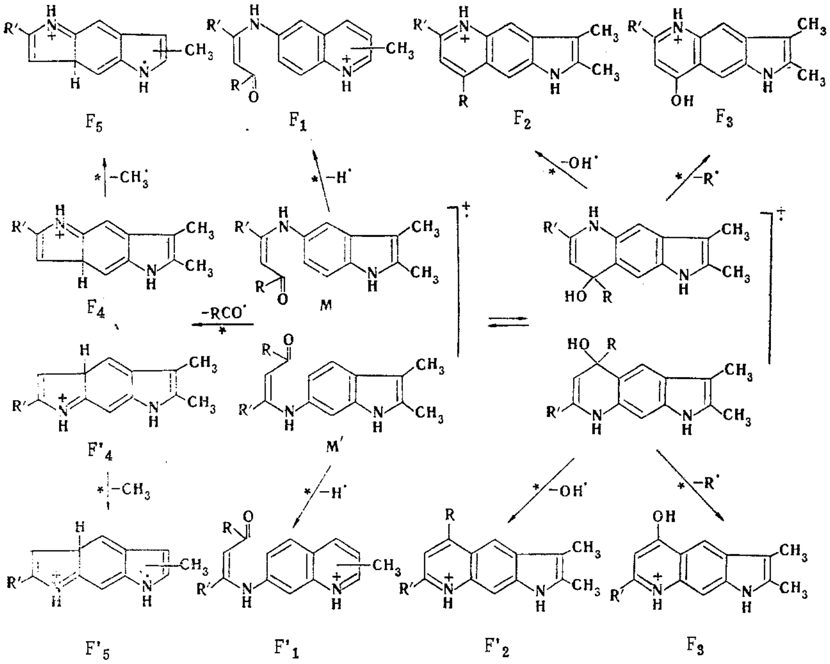


Ia, b IIa-f

Ia 5-NH_2; b 6-NH_2; IIa 5-NH, R'=R=CH_3; b 6-NH, R'=R=CH_3; c 5-NH, R'=R=C_6H_5; d 6-NH, R'=R=C_6H_5; e 5-NH, R'=CH_3, R=C_6H_5; f 6-NH, R'=CH_3, R=C_6H_5

An alternative reaction through one or the other keto groups could have been assumed for IIe and IIf. However, a chromatographic study demonstrated the individuality of the product; this eliminated the assumption of the formation of a mixture. The mass spectra of IIa-f (Table 1) are characterized primarily by elimination of RCO• from the molecular ion. In this case an acetyl group is split out from IIa and IIb, whereas a benzoyl group is split out from IIc and IId. Since the molecular ions of IIe and IIf split out a benzoyl group, it can be asserted that this group is found at the end of the side chain, and, consequently, the condensation of both 5- and 6-aminoindoles (Ia or Ib) with benzoylacetone proceeds with the participation of the acetyl group rather than the benzoyl group.

The molecular peak is not the maximum peak for any of these compounds, and fragmentation of the molecular ion proceeds via five principal pathways: elimination of a hydrogen atom, elimination of an OH• group, elimination of an R• radical, successive elimination of RCO• and CH_3• radicals, and formation of RCO^+ and R^+ ions (see the scheme below).



The formation of $[M-H]^+$ ions is evidently due to the indole portion of the molecule, i.e., one of the methyl hydrogen atoms is eliminated with expansion of the pyrrole ring. This process is one of the principal processes for the mass spectrometric fragmentation of mono- and polymethylindoles [7]. The processes involving splitting out of OH• and R• radicals are confirmed in all cases by peaks of metastable ions and show that the ions of the enamine ketones are rearranged to the corresponding dihydroquinolines (linear or angular) to give F_2 and F_3 ions. Successive elimination of RCO• and CH_3• radicals by the molecular ions in all of the mass spectra is also confirmed by the corresponding metastable transitions. Ions of the $[RCO]^+$ (F_6) type with R=C_6H_5 (benzoyl cations) have higher intensities than acetyl cations. The benzoyl cations undergo subsequent fragmentation with successive splitting out of CO and C_2H_4 (metastable ions at m/e 56.5 and 33.7), whereas the acetyl cations undergo fragmentation to give CH_3^+ (F_7) ions.

Thus the fragmentation of enamino ketones IIa-f under the influence of electron impact follows the general scheme, but the mass spectra of the 5- and 6-isomers differ markedly. The stabilities of the molecular ions

TABLE 1. Mass Spectra of IIa-f

Compound	m/e value (relative %) of the ion peaks*						
IIa	243 (12,8)	242 (100)	241 (8,5)	288 (7,6)	227 (65,6)	226 (8,8)	225 (44,1)
	212 (6,4)	211 (6,1)	200 (11,3)	199 (82,5)	198 (9,5)	197 (8,5)	285 (16,8)
	184 (78,5)	183 (21,4)	182 (7,3)	160 (7,6)	159 (8,8)	158 (14,9)	145 (9,1)
	144 (21,4)	115 (9.5)	112 (7,0)	92 (11,9)	84 (12,5)	77 (9,8)	43 (48,7)
	59 (11,6)	15 (64.0)					
IIb	243 (16,7)	242 (100)	241 (8,3)	227 (36,6)	225 (18,7)	212 (11,7)	211 (12,1)
	200 (6,6)	199 (38,0)	198 (6,3)	197 (6,3)	185 (12,1)	184 (36,6)	183 (14,6)
	160 (10,4)	159 (14.6)	158 (19,2)	144 (12,1)	143 (12,1)	115 (6,3)	113 (5,8)
	105 (6,6)	85 (6,3)	84 (20,8)	43 (33,4)	15 (53,2)		
IIc	367 (4,6)	366 (22,0)	365 (4,3)	349 (42,0)	289 (18,6)	262 (14,7)	261 (100)
	260 (11,9)	247 (26,4)	246 (94,5)	245 (12,4)	144 (11,2)	143 (7,7)	115 (7,0)
	105 (41,0)	91 (6.3)	81 (6,2)	78 (10,9)	77 (51,0)		
IId	367 (24,8)	366 (100)	365 (11,5)	349 (22,8)	289 (14,7)	362 (18,7)	261 (93,6)
	260 (12,5)	259 (8,7)	247 (13,8)	246 (55,0)	245 (12,5)	159 (16,2)	158 (13,8)
	144 (11,3)	143 (8,7)	105 (75,0)	91 (6,3)	77 (59,4)		
IIe	305 (16,3)	304 (80,4)	303 (29,4)	289 (9,8)	288 (9,5)	287 (39,1)	226 (13,7)
	226 (13,7)	200 (13,1)	199 (100)	198 (9,8)	197 (4,9)	185 (9,8)	184 (55,1)
	183 (16.7)	160 (9,2)	159 (10,1)	158 (6.7)	145 (9,5)	144 (19,6)	143 (16,4)
	115 (8,2)	105 (80,2)	91 (9,2)	77 (48,4)			
IIf	305 (19,5)	304 (100)	303 (31,6)	289 (7,8)	288 (7,0)	287 (31.6)	226 (13,3)
	200 (10,9)	199 (95,7)	198 (9,0)	185 (9,8)	184 (54,6)	183 (19.2)	160 (10,1)
	159 (11,7)	158 (7,8)	145 (7,8)	144 (19,2)	143 (15,2)	115 (7,8)	105 (82,4)
	77 (46,8)						

* The ion peaks with intensities up to 5% of the maximum peak are presented.

TABLE 2. W_M^8 Values and Intensity Ratios of the Molecular and Fragment Ions in the Mass Spectra of IIa-f*

Compound	W_M^8	I_{M-1}/I_M	I_{M-OH}/I_M	I_{M-R}/I_M	I_{M-RCO}/I_M	$\frac{I_{M-RCO-15}}{I_{M-RCO}}$	I_{RCO}/I_M	I_{F_7}/I_{F_6}
IIa	17,0	0,09	0,44	0,64	0,83	0,94	0,49	1,60
IIb	30,8	0,08	0,19	0,37	0,38	0,97	0,33	1,31
IIc	5,9	0,20	1,90	0,85	4,54	0,95	1,87	1,25
IId	23,1	0,11	0,23	0,15	0,94	0,59	0,75	0,79
IIe	17,0	0,37	0,49	0,17	1,24	0,55	0,99	0,61
IIf	18,0	0,32	0,32	0,14	0,96	0,57	0,82	0,57

*The overall intensity of the peaks of the examined ions is ~ 70-80% of the total ion current.

with respect to electron impact (W_M^8)* and the intensity ratios (I) of the principal ions in the mass spectra of the investigated compounds are presented in Table 2. The 6-isomers have considerably greater stability with respect to electron impact than the 5-derivatives. On the other hand, the fragment ions in the mass spectra of the 5-enaminoketoindoles have higher stabilities, and this shows up particularly markedly for the F_2-F_4 ions. This can be explained by resonance stabilization [8]. In the case of the F'_n ions the 2,3-methyl groups do not participate in the resonance transformations, whereas in the case of F_n ions the conjugation chain is longer and, in addition, the methyl groups that participate in resonance promote delocalization of the positive charge; this evidently is responsible for the relatively high intensities of these ions. The differences in the I_{RCO}/I_M ratios should be ascribed to energy factors [9] specifically, since these values are lower for the 6-isomers, in this case the $[RCO]^+$ ions are formed with higher energies and undergo fragmentation at higher rates to give R^+ ions; this follows from a complex examination of the I_{RCO}/I_M and I_R/I_{RCO} values for isomeric pairs. The noted differences in the relative intensities of the molecular and fragment ions are also observed for IIe and IIf, but they show up more weakly here. Nevertheless their mass spectra make it possible to reliably distinguish and identify the isomeric pairs.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in DMSO–acetone (1 : 2) were recorded with a Varian S-60T spectrometer with hexamethyldisiloxane as the internal standard. The mass spectra were obtained with

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* The W_M^8 values are the fractions of the molecular ions in the total current of the M^+ and F_n (n= 1-7) ions.

TABLE 3. 3-(Indolylamino)vinyl Ketones (IIa-f)

Compound	Name	Starting diketone	Preparative method	R_f	mp, °C	Empirical formula	Found, %		Calc., %		UV spectrum		PMR spectrum, δ, ppm								Yield, %
							C	H	C	H	λ_{max} (nm)	lg ε	NH_{amin}	NH_{ind}	7-H	6-H	5-H	4-H	$H_{C_6H_5}$	H_{vin}	
IIa	4-[(2,3-Dimethyl-5-indolyl)amino]pent-3-en-2-one	$CH_3COCH_2COCH_3$	A	0,37	131—131,5	$C_{15}H_{18}N_2O$	74,1	7,6	74,4	7,4	223 315	4,64 4,38	12,46 s	10,45 s	7,06 d $J_{7,6}=8$ Hz	6,62 q	$J_{6,4}=2$ Hz	6,98 d		5,00 s	80
IIb	4-[(2,3-Dimethyl-6-indolyl)amino]pent-3-en-2-one	$CH_3COCH_2COCH_3$	A	0,28	147	$C_{15}H_{18}N_2O$	74,2	7,6	74,4	7,4	223 315	4,64 4,68	12,45 s	10,28 s	6,97 d $J_{7,5}=2$ Hz		6,67 q $J_{5,4}=8$ Hz	7,26 d		5,07 s	85
IIc	1,3-Diphenyl-3-[(2,3-dimethyl-5-indolyl)amino]prop-2-en-1-one	$C_6H_5COCH_2COC_6H_5$	B	0,77	185—186	$C_{25}H_{22}N_2O$	81,8	6,0	82,0	6,0	230 290 385	4,44 4,16 4,29	13,09 s	10,59 s	7,00 d $J_{7,5}=8$ Hz	6,48 q	$J_{6,4}=2$ Hz	6,85 d	8,10—7,25 m	6,07 s	68
IId	1,3-Diphenyl-3-[(2,3-dimethyl-6-indolyl)amino]prop-2-en-1-one	$C_6H_5COCH_2COC_6H_5$	B	0,77	178—179	$C_{25}H_{22}N_2O$	81,9	6,0	82,0	6,0	235 330 400	4,55 4,24 4,40	13,12 s	10,24 s	6,73 d $J_{7,5}=2$ Hz		6,50 q $J_{5,4}=8$ Hz	7,10 d	8,10—7,25 m	6,05 s	75
IIe	1-Phenyl-3-[(2,3-dimethyl-5-indolyl)amino]but-2-en-1-one	$C_6H_5COCH_2COCH_3$	B	0,50	169—170	$C_{20}H_{20}N_2O$	79,1	6,6	78,9	6,6	235 285 350	4,42 4,03 4,32	13,23 s	10,83 s	8,10—6,75 m					6,00 s	66
IIf	1-Phenyl-3-[(2,3-dimethyl-6-indoly)amino]but-2-en-1-one	$C_6H_5COCH_2COCH_3$	B	0,49	160—161	$C_{20}H_{20}N_2O$	79,0	6,5	78,9	6,6	237 285 360	4,42 3,83 4,26	13,20 s	10,66 s	8,10—6,70 m					5,97 s	74

an MKh-1303 mass spectrometer with direct introduction of the samples into the ion source at an ionization energy of 50 eV and an emission current of 1.5 mA at 70-220°. The electronic spectra of ethanol solutions of the compounds were recorded with a Cary-15 spectrophotometer. The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. Chromatography was carried out on Silufol in a benzene—ethyl acetate system (5 : 1). 2,3-Dimethylindoline was obtained by the method in [10] and had bp 234-236° and n_D^{25} 1.557 (bp 224-236° and n_D^{25} 1.556 [10]).

2,3-Dimethyl-6-nitroindole. A 7.8-g (123 mmole) sample of concentrated nitric acid (sp. gr. 1.5) was added in small portions with stirring and cooling to 0-5° to a solution of 18 g (122.7 mmole) of freshly distilled 2,3-dimethylindoline in 100 ml of concentrated sulfuric acid, after which the mixture was allowed to stand at room temperature for 2 h. It was then poured over ice, and the aqueous mixture was made alkaline with 10% ammonium hydroxide. The nitroindoline was extracted with five 100-ml portions of ether, the ether was removed by distillation, and the residue was vacuum fractionated with collection of the fraction with bp 188-192° (15 mm).

A 29-g (132 mmole) sample of chloranil was added to a solution of this fraction in 230 ml of p-xylene, and the mixture was refluxed with constant stirring for 7 h. It was then cooled and treated with concentrated ammonium hydroxide, and the resulting precipitate was removed by filtration. The xylene layer in the filtrate was separated and dried, and the xylene was removed by distillation. The resulting 2,3-dimethyl-6-nitroindole was recrystallized from xylene to give 9 g (39%) of a product with mp 140-141° (mp 142° [11]).

2,3-Dimethyl-5-nitroindole. A solution of 2.5 g (21 mmole) of potassium nitrate in 20 ml of 95% sulfuric acid was added with cooling and stirring to 3 g (21 mmole) of 2,3-dimethylindole in 20 ml of 95% sulfuric acid at such a rate that the temperature of the mixture did not rise above 8°. Ten to fifteen minutes after mixing, the mixture was poured with stirring over ice. The resulting precipitate was removed by filtration, washed thoroughly with water, and air dried to give 3.4 g (80%) of a product with mp 184-186° (from methanol) (mp 185-187° [11]).

2,3-Dimethyl-5-aminoindole. A catalytic amount of Raney nickel was added to a solution of 0.95 g (5 mmole) of 2,3-dimethyl-5-nitroindole in 100 ml of methanol, after which 8 ml (150 mmole) of hydrazine hydrate was added with stirring. The mixture was heated and stirred for 1.5 h. At the end of the reaction, the hot mixture was filtered to remove the catalyst, and the methanol was removed from the filtrate by distillation. The solid residue was recrystallized from 50% aqueous alcohol to give 0.51 g (64%) of a product with mp 174° (from benzene) (mp 173-174° [12]).

2,3-Dimethyl-6-aminoindole. This compound, with mp 117-118° (from benzene) (mp 117-118° [12]), was similarly obtained in 85% yield from 2,3-dimethyl-6-nitroindole.

General Method for the Preparation of II.* A) A 0.32-g (2 mmole) sample of aminoindole was dissolved in 3 g (30 mmole) of acetylacetone, and the mixture was refluxed for 30 min. After all of the aminoindole had been converted (chromatographic monitoring), the excess acetylacetone was removed by vacuum distillation. The solid slightly yellow residue was recrystallized from aqueous alcohol.

B) A mixture of 0.5 g (3.1 mmole) of aminoindole and 0.9 g (4 mmole) of dibenzoylmethane or 0.65 g (4 mmole) of benzoylacetone was heated at 160-165° for 2 h. The condensation product was purified with a column filled with activity II aluminum oxide with elution by benzene—ethyl acetate (8 : 1).

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*The preparative conditions and the physical constants of IIa-f are presented in Table 3.

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EFFECT OF ARYL SUBSTITUENTS ON THE RATE OF DARK DECOLORIZATION OF PHOTOCHROMIC SPIROCHROMENES OF THE INDOLINE SERIES

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The introduction of aryl substituents in the 3' and 7 positions of the indoline spirochromene molecule gives rise to a certain amount of slowing down of dark decolorization in toluene and dioxane; similar changes in the 5', 6, and 8 positions do not change the rate appreciably.

It is necessary to know the principles that link the structures of compounds with their photochromic properties for the directed creation of photochromic materials. These principles are presently being studied intensively in the case of a number of indoline spirochromenes, the most promising class of photochromic substances.

We have previously established that the introduction of aryl substituents in the 5' and 6-8 positions of the spirochromene molecule leads to a bathochromic shift of the absorption band of the photomerocyanine to the visible region [1-3], whereas the introduction of aryl substituents in place of methyl substituents in the 3' position does not give rise to substantial spectral changes [4, 5]. It seemed of interest to ascertain how the indicated structural changes would affect such an important characteristic of the photochromic behavior of the spirochromene as the rate constant for dark decolorization. In addition to a direct evaluation of the lifetime of the photocolored form, a study of the kinetics of the dark reaction also makes it possible to evaluate the change in the light sensitivity of the photochromic system [6] and thus to obtain an idea regarding the complex change in the spectral and kinetic parameters of the photochromic material as the structure of the spirochromene changes.

With this in mind, we measured the rate constants and activation parameters of the dark decolorization of photocolored solutions of 15 indoline spirochromenes containing a phenyl or p-methoxyphenyl substituent in various positions. In most of the investigated cases we observed good compliance of the investigated reaction with a first-order kinetic equation: The scatter in the rate constants for individual points of the kinetic curve did not exceed 10% up to practically total completion of the decolorization reaction. Dioxane and toluene, which are usually employed for spectral-kinetic studies of spirochromenes, were used as the solvents.

The results are presented in Table 1. The rate constants that we determined for spirochromenes I and XII agreed satisfactorily with the literature data.

A comparison of the rate constants and the activation parameters for spirochromenes I and II and III and IV makes it possible to establish that the introduction of a phenyl substituent in the 6 and 8 positions of the spirochromene molecule does not give rise to appreciable changes in the kinetic behavior of the photochromic

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