INVESTIGATION OF THE FISCHER CYCLIZATION OF DIARYLHYDRAZONES AND RELATED SECONDARY HYDRAZONES

II.* NEW EXAMPLES OF THE EFFECT OF THE STRUCTURE OF THE ARYL GROUP ON THE ORIENTATION DURING REARRANGEMENT

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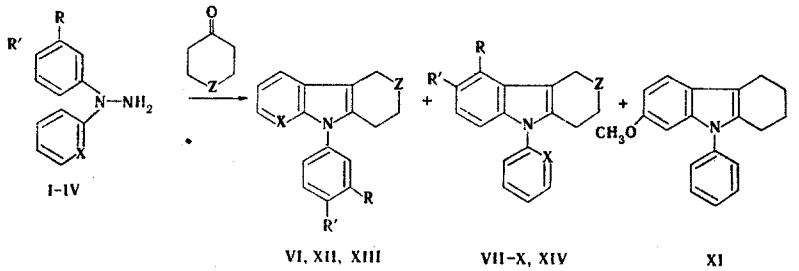
It was established by the method of intramolecular competition during the formation of an indole ring from N,N-diarylhydrazones in acidic media that aryl groups with p-ethoxycarbonyl or m-methoxy groups are less reactive than unsubstituted phenol, whereas the 2-naphthyl group is more reactive than the phenyl group. The results are examined from the point of view of the qualitative classification of the substituents with respect to their electronic effects.

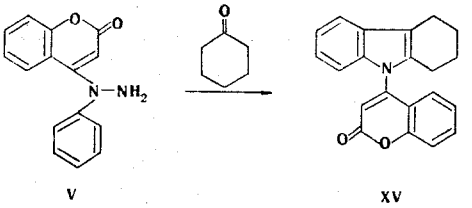
In the case of competitive cyclization of N,N-diarylhydrazones of cyclohexanone and related ketones electron-donor substituents (CH_3O and CH_3) in the para position of the phenyl ring facilitate cyclization as compared with the hydrogen atom [1].

In the present paper we present the results of indolization of a number of other diarylhydrazones of cyclic ketones obtained without isolation in the free state from hydrazines I-IV and cyclohexanone, as well as from hydrazine IV and tetrahydro-4-thiapyrone; in addition, we accomplished the condensation of hydrazine V with cyclohexanone. Substituted indoles VI-XV were identified among the reaction products. In the case of the reaction of hydrazines I-III the ratio of indole compounds (in the case of good overall yields) was determined by PMR and IR spectroscopy.



I-IV VI, XII, XIII VII-X, XIV XI

VI—VIII, X, XII—XIV Z=CH_2; IX Z=S; I, VI, VII R=H, R′=$COOC_2H_5$, X=CH; II, X, XII R=OCH_3, R′=H, X=CH; III, XIII, XIV R+R′= benzo, X=CH; IV, VIII, IX R=R′=H, X=N



V XV

* See [1] for communication I.

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A p-ethoxycarbonyl group appreciably passivates the benzene ring: VI and VII were obtained in 85 and 15% relative yields. In preparative experiments on the indolization of the hydrazones from IV and cyclohexanone or tetrahydrothiapyrone 74% VIII or 61% IX was obtained. The isomeric substituted indoles were not detected in the reaction products. The low reactivity of the pyridine ring (particularly in the protonated form) is well known [2], and additional proof of the structure of VIII and IX was therefore unnecessary.

It has been established by kinetic studies [3, 4] that cyclohexanone 3-methoxyphenylhydrazone is cyclized more slowly than the unsubstituted phenylhydrazone (the ratio of the rate constants is 0.64-0.84 : 1). Our experiments on the condensation of hydrazine II with cyclohexanone are in agreement with this: isomers X, XI, and XII were obtained in 20, 26, and 54% relative yields, which corresponds to a ratio of 0.85 : 1 of the overall yield of cyclization products with respect to the methoxyphenyl group to the yield of the N-methoxyphenyl derivative of indole. In [3] on the basis of the literature data [4-6] and his own data on the kinetics of indolization of ring-substituted cyclohexanone arylhydrazones (in 60% aqueous methanol with excess HCl and ketone at 43.2°C), Elgersma concluded that the rate of formation of indoles depends on the basicity of the 1-N atom of the hydrazone, which is predetermined by the basicity of the corresponding aniline. However, the rate constants for the cyclization of 1- and 2-naphthylhydrazones and the 2-methylphenylhydrazone were found to be higher than that of the phenylhydrazone, although the basicities of the corresponding arylamines are lower than that of aniline (pK_a) 3.92, 4.11, 4.39, and 4.58, respectively). According to our experiments, the 2-naphthyl residue also displays high reactivity (by a factor of four, with allowance for the partial reactivity) as compared with the phenyl residue: the reaction mixture consisted of 33% isomer XIII and 67% isomer XIV. The third isomer (with a benzocarbazole structure) was not detected.

4-Aminocoumarin is the heteroaromatic analog of 1-aminonaphthalene, but it has a considerable deficit of π-electron density at 4-C (its basicity is comparable to the basicities of amides) [7, 8] and excess negative charge on 3-C. In the case of indolization of the hydrazone from hydrazine V we ascertained that the 3 position of the coumarin residue has lower reactivity (it is unlikely that this is due to sufficiently complete secondary protonation of the carbonyl group) than the ortho position of the phenyl rings: X, which was identified from the 3-H signal of the pyrone ring (δ 6.3 ppm, in CCl_4), was isolated in 64% yield.

The results that we obtained here and previously [1] with respect to the determination of the relative orienting abilities of substituents in the aryl portion of diarylhydrazones coincide qualitatively with the relative kinetic characteristics of the effect of the corresponding substituents in monoarylhydrazones [3-6]. The data of other researchers on the cyclization of diarylhydrazones are also in agreement with the indolization kinetics. A chlorine atom in the 4 position of cyclohexanone N,N-diphenylhydrazone and a methoxy group in the 2 position of pyruvic acid diphenylhydrazone slow down cyclization in the substituted phenyl ring [9, 10]. In [10] it was assumed that the cyclization of hydrazine I with pyruvic acid leads only to a benzene ring-unsubstituted indole. The 4-methoxy group activates the ring [9, 10].* The tetrahydrocarboline structure [11] was assigned to the product of indolization of IV with 1-methyl-4-piperididone, which was obtained in a preparative experiment. It has been assumed that the cyclization of N-phenyl-N-(3,5-dimethylphenyl)hydrazones takes place in the substituted ring [12].

Hence we arrive at the following important conclusions. 1) Since the nitrogen atoms and the ene portion in N,N-diarylhydrazones are common to both aryl groups, the relative orienting abilities of the substituents in the aryls should not be directly determined by the rates of the tautomeric transformations and the equilibrium constants of the protonated forms, whereas in the case of indolization of monoarylhydrazones the rate of rearrangement may depend directly on the degree of protonation, the ratio of the nonidentically protonated forms, the rates of tautomerization, the equilibrium constants of the various forms, etc. 2) The rather good qualitative agreement between the results of estimation of the effect of substituents on the relative reactivities of N,N-diarylhydrazones and N-monoarylhydrazones during acid-catalyzed indolization (at least within the scope of the reactions investigated in this respect) constitutes evidence that the rearrangement proper is a slower step than protonation and tautomerization; moreover, the tautomeric equilibrium and protonation constants in various hydrazones with an identical carbonyl component evidently do not change under the influence of substituents to such an extent that the characteristic effect of the substituents on the rate of rearrangement of the enehydrazine is masked. In contrast to this, the structural peculiarities of the carbonyl components (in the case of an identical hydrazine portion) cannot markedly affect the rates of rearrangement not only because of the different reactivities of the ene fragment during formation of a new C–C bond but also because of the shift

* The experimental conditions, the analytical methods, and the characteristics of the reaction products were not described in the brief communication (theses) [10].

of the tautomeric equilibrium, which is known from numerous preparative experiments, semiquantitative determinations [13, 14], and kinetic measurements [6].

A fundamentally different rearrangement mechanism was expressed in [3]: the hydrazone form rather than the enehydrazine form undergoes this transformation through a noncyclic transition state, and "the factors that are favorable for achieving the transition state are: a relatively high electron density on the 1-N atom and a relatively reduced electron density on the 2-C atom of the aromatic ring in the transition state" [3].

The results of cyclization of variously substituted (in the aromatic rings) N,N-diarylhydrazines and some other facts do not confirm the proposed mechanism [3], but the conclusion that in the investigated cases the rearrangement step proceeds more slowly than all of the preceding equilibrium processes [3] must be considered to be correct.*

After the criticism [15] of the mechanism of the rearrangement of arylenehydrazines that includes electrophilic attack of the ene fragment on the aromatic ring, no new approaches that explain, at least on a qualitative level, the dependence of the relative rates of rearrangement of enehydrazines on the character of the substituents appeared. One can therefore draw attention to some factors the consideration of which would enable one to at least classify the substituents and their position with respect to their effect on the ease of rearrangement, regardless of the sort of fine mechanism of bond cleavage and bond formation that is involved in the process. It must be assumed that an increase in the negative charge on the 2-C atom of the aromatic ring† will most effectively promote the rearrangement only when it is a consequence of transmission of the electron density directly from the 1-C atom. One must therefore take into account the effect of the substituents on the charge density not only with respect to the 2-C atom but also (and particularly) with respect to the 1-C atom.

The 4-CH_3O group substantially raises the electron density on 1-C atom and somewhat lowers the negative charge on the 2-C atom (the pK_a values of m- and p-anisidines are 4.20 and 5.29). The 3-CH_3 and 4-CH_3 substituents also accelerate the rearrangement, raising the negative charge on the 1-C and 2-C atoms (the pK_a values of m- and p-toluidines are 4.69 and 5.12); the rate of indolization of the p-tolylhydrazone is higher than that of the meta isomer [3]. The 2-CH_3O group somewhat deactivates the 2-C position and has an unfavorable effect on the charge density on 1-C (the pK_a value of o-anisidine is 4.49). The 3-CH_3O group activates the para position with respect to it but passivates the ortho position and, what is more important, lowers the electron density on 1-C. As a result, the ring as a whole is somewhat deactivated (with allowance for a lesser degree of steric hindrance than presented above). The introduction of two CH_3O groups in both meta positions of one of the phenyl rings of pyruvic acid N,N-diarylhydrazone ensures indolization only of the substituted phenyl ring [10], in all likelihood due to predominance of the concerted dynamic effect of the methoxy groups. The "anomalous" reactivities of 1- and 2-naphthylhydrazones are easily explained by the increased bond order [16], i.e., by the increased electron density in the C_1-C_2 zone of naphthalene. In the case of the o-tolylhydrazone, one should take into account the nonconformity between the experimentally determined ionization constant of o-toluidine and the electron density in the ortho position: because of the ortho effect, the basicity is reduced by 0.6 pK_a units (for example, see [16]). o-Tolylhydrazine is only slightly more basic than phenylhydrazine [17]; the pK_a values, respectively, are 5.32 and 5.27 (the ortho effect on the basicity of the β-NH_2 group is not manifested here). This fact must also be borne in mind during evaluation of the orienting ability of a m-methyl group (see above). Electron-acceptor substituents in any position of the aromatic ring have a deactivating effect (for example, the pK_a values for m- and p-ethoxycarbonylanilines and m- and p-chloroanilines are, respectively, 3.64, 2.38, 3.34, and 3.98). The dynamic effects of substituents should probably be manifested in the case of sufficiently high initial perturbation of the active centers [18]. All of this indicates that even a single and very simple change in the structure of the arylhydrazine portion of the molecule (including the 1-N atom) is capable of giving rise to effects that act in the opposite direction.

One cannot yet give an unambiguous answer to the question as to whether acid catalysis occurs in the step involving rearrangement of the enehydrazine by means of the method of competitive closing of the indole ring in N,N-diarylhydrazones. However, it has been convincingly demonstrated [13] in the case of the indolization of N,N^1-dimethyl-N-phenylhydrazines with various ketones and aldehydes that acids markedly accelerate the rearrangement of systems with a fixed ene portion. It is usually assumed that in the case of acid-catalyzed indo-

* In the case of a sufficiently high degree of protonation of the hydrazones (acid concentration 0.6 M, pK_a 3 for cyclohexanone phenylhydrazone) the difference in the reaction rates should not depend on the concentration of the protonated form [3].

† For convenience, we will designate only the atom in the ortho position with which a new C–C bond is formed as the 2-C atom; regardless of this, the numbering of the substituents is carried out in the usual order.

lization the hydrazone is protonated at the 2-N atom (see also [13], in which the basicities of aniline and aminovinyl structures are compared). However, there have often been cases in which the basicity of the vinylamine portion of the molecule is undoubtedly lower than the basicity of the aniline portion (for example, in arylhydrazones of 1,3-dicarbonyl compounds). Consequently, in the general case acid catalysis will be realized by protonation of the 1-N or 2-N atom in arylhydrazines, for which reason, the effect of a substituent, it seems to us, sometimes may be reversed.*

The considerably less expressed effect of substituents in the aromatic ring during the indolization of arylhydrazones with respect to the effects of the corresponding substituents in ordinary electrophilic aromatic substitution reactions [16] should be explained by the fact that in the first case the reaction rate is evidently controlled not only by the charge on the terminal atoms of the system but is also substantially dependent on the energy (determined by many factors) of cleavage of the N–N bond and the possibilities of effective participation of the C_1-C_2 fragment in the cyclic transition state†; however, on the whole, the process is formally described as an orbitally controlled recyclization reaction with a [3,3]sigmatropic shift [15, 22, 23].

Thus our proposed method of competitive closing of the indole ring of N,N-diarylhydrazones makes it possible to directly evaluate the orienting effect of substituents in the aryl portion of the molecule on the step involving the rearrangement of the enehydrazine form and facilitates uncovering of the steps that determine the rate of the entire indolization process and clarification of some aspects of the mechanism of the rearrangement of enehydrazines and related systems.

EXPERIMENTAL

The PMR spectra of the compounds were recorded with Varian T-60 and Brüker WN-90 spectrometers. The IR spectra of CS_2 or CCl_4 solutions of the compounds were recorded with a Perkin–Elmer 457 spectrometer. The UV spectra of alcohol solutions (10^{-5}–10^{-4} M) of the compounds were obtained with a Perkin–Elmer 420 spectrophotometer. The general method for the determination of the ratios of the indolization products, the monitoring of the purity of the individual substances, and the qualitative monitoring of the compositions of the isomeric compounds of the indole series have been previously described [1]. A loose layer of Al_2O_3 [activity II or III, CCl_4–benzene (4:1) or chloroform] and Silufol UV-254 plates (chloroform) were used for thin-layer chromatography (TLC).

The individual indole derivatives (VI, VIII, IX, XIV, and XV) were isolated from the reaction mixtures in a number of cases, whereas VII, XI, and XIV were obtained by independent methods (see Table 1). Compounds X, XII, and XIII were obtained as references by independent methods and were characterized only by their PMR and IR spectra. The following is a list of the compounds, solvents, and chemical shifts of the protons of the groupings used for the analysis of the ratios of the indolization products: X, benzene, 3.46 (5-CH_3O); XI, ben-

TABLE 1. Compounds VI-IX, XI, and XV

Compound	bp (mm) or mp,[a] °C	Found, %			Empirical formula	Calculated, %		
		C	H	N		C	H	N
VI[b]	98–99	78,3	6,6	4,2	$C_{21}H_{21}NO_2$	78,8	6,8	4,4
VII[c]	83–84	79,0	6,6	4,6	$C_{21}H_{21}NO_2$	78,8	6,8	4,4
VIII[b]	52,5–54	82,2	6,6	11,5	$C_{17}H_{16}N_2$	82,2	6,5	11,3
IX[b]	92–93	72,3	5,3	10,3	$C_{16}H_{14}N_2S$[d]	72,1	5,3	10,5
XI[c]	205–207 (2)	83,0	7,2	4,9	$C_{19}H_{19}NO$	82,9	6,9	5,0
XIV[b,c]	135–136	88,5	6,6	4,9	$C_{22}H_{19}N$	88,8	6,4	4,7
XV[b]	172–174	80,5	5,5	4,6	$C_{21}H_{17}NO_2$	80,0	5,5	4,4

[a]Compounds VI, XIV, and XV were recrystallized from alcohol, and VII, VIII, and IX were recrystallized from petroleum ether.
[b]These compounds were isolated from the reaction mixtures.
[c]These compounds were obtained by an independent method.
[d]Found: S 11.8%. $C_{16}H_{14}N_2S$. Calculated: S 12.0%.

* See [19] for the experimentally established mechanism of the benzidine rearrangement in the case of double protonation of the N and C atoms.

† The effect of para substituents on the rate of Claisen rearrangement could not be correlated [20, 21], and it was correctly noted in [20] that in addition to the effect of a substituent on the para and meta positions of the benzene ring, one would also have to take into account its effect on the ease of cleavage of the C–O bond.

zene, 3.3 (7-CH_3O); XII, benzene, 3.1 (3'-CH_3O); VI,* CCl_4, 8.0 and 8.27 (signal from two basic components of 3-H and 5-H of the AA^1MM^1 system in the 4-ethoxycarbonylphenyl group; the reciprocal two-component signal from 2'-H and 6'-H is found at 7.4 ppm); VII, CCl_4, 7.6 [7-H, q, J_1 = 9 Hz, J_2 = 2 Hz; the reciprocal signals (d 8-H, J_1 = 9 Hz, and 5-H, J_2 = 2 Hz) are found at δ 7.6 and 7.0 ppm, respectively]; XIII, CCl_4, 2.45 and 2.65 (4H, unresolved m, 4-H and 1-H); XIV, CCl_4, 2.55 (2H, 11-H, m); 3.15 (2H, 8-H, m), 7.7 and 8.2 (1-H and 4-H, two q with J_1 = 7.5 Hz and $J_2 \approx 2$ Hz for each).† The isomer ratio established by IR spectroscopy from the peak at 698 cm^{-1} for XIV and the peak at 480 cm^{-1} for XIII was in agreement (±2%) with the ratio obtained from the PMR spectral data.

N-Phenyl-N-(p-ethoxycarbonylphenyl)amine (XVI). A mixture of 30 g (0.182 mole) of ethyl p-aminobenzoate, 80 g (0.384 mole) of iodobenzene, 38 g (0.275 mole) of calcined potassium carbonate, 2 g (0.02 mole) of potassium iodide, and 1 g of copper powder was heated with stirring at 180-190°C for 9 h, after which the iodobenzene was removed by steam distillation, and the residue was extracted with benzene. The extract was evaporated to give 10 g (27%) of amine XVI with mp 108-110°C (from alcohol). Found: C 74.9; H 6.3; N 5.9%. $C_{15}H_{15}NO_2$. Calculated: C 74.7; H 6.2; N 5.8%.

N-Phenyl-N-(p-ethoxycarbonylphenyl)-N-nitrosoamine (XVII). This compound, with mp 71-72°C (from alcohol), was obtained in 93.5% yield from amine XVI by the method in [1]. Found: C 66.6; H 5.2; N 10.2%. $C_{15}H_{14}N_2O_3$. Calculated: C 66.6; H 5.2; N 10.4%.

N-(p-Ethoxycarbonylphenyl)-N-phenylhydrazine (I) Hydrochloride. A) Acetic acid (10 ml) was added with stirring and cooling (10°) in the course of 2 h to a mixture of 5.7 g (0.021 mole) of nitrosoamine XVII and 15 g (0.23 g-atom) of zinc dust in 80 ml of alcohol, after which the mixture was stirred for 1 h. It was then filtered, and the mother liquor was vacuum evaporated. The residue was dissolved in water, and the solution was made alkaline with ammonia and extracted with either. The extract was dried and treated with a solution of hydrogen chloride in ether. Workup gave 0.6 g (10%) of the hydrochloride with mp 146-148°C. Found: C 61.2; H 5.8; Cl 12.1; N 9.7%. $C_{15}H_{16}N_2O_2 \cdot HCl$. Calculated: C 61.5; H 5.8; Cl 12.1; N 9.6%.

B) Concentrated ammonium hydroxide (25 ml) was added in portions at 0°C to a mixture of 6.5 g (0.024 mole) of nitrosoamine XVII, 10.8 g (0.12 mole) of ammonium acetate, and 5 g (0.077 g-atom) of zinc dust in 100 ml of alcohol. After 1 h, another 5 g of zinc dust was added, and the mixture was stirred for 3 h. It was then filtered, and the filtrate was vacuum evaporated. The residue was made strongly alkaline with sodium hydroxide solution, and the mixture was worked up as indicated above to give 1 g (14%) of the hydrochloride of I.

N-(m-Methoxyphenyl)-N-phenylhydrazine (II) Hydrochloride. This compound, with mp 142-142.5°C (dec., from isopropyl alcohol with ether), was obtained in 73% yield from N-(m-methoxyphenyl)-N-phenylamine by the method in [1] without purification of the N-(m-methoxyphenyl)-N-phenyl-N-nitrosoamine. Found: C 62.4; H 6.0; Cl 14.1; N 11.2%. $C_{13}H_{14}N_2O \cdot HCl$. Calculated: C 62.3; H 6.1; Cl 14.1; N 11.3%.

N-Phenyl-N-(4-coumarinyl)hydrazine (V). A 1.34-g (0.056 mole) sample of sodium hydride was added to a solution of 3 g (0.028 mole) of phenylhydrazine in 25 ml of absolute benzene, and the mixture was refluxed for 1.5 h. It was then cooled and treated with a solution of 5 g (0.028 mole) of 4-chlorocoumarin in 30 ml of absolute benzene, and the mixture was refluxed for 1 h, after which it was poured into water. The benzene solution was washed twice with 7% potassium hydroxide solution and water and extracted with 7% hydrochloric acid solution. The aqueous solution was washed with 2 N sodium carbonate solution and worked up to give 1.15 g (16%) of hydrazine V with mp 166-167.5°C (from absolute alcohol). Found: C 71.7; H 4.8; N 11.3%. $C_{15}H_{12}N_2O_2$. Calculated: C 71.4; H 4.8; N 11.1%.

N-(2-Naphthyl)-N-phenylhydrazine (III) Hydrochloride. This compound was obtained by the method in [23].

N-Phenyl-N-(2-pyridyl)hydrazine (IV). This compound was obtained by the method in [24].

Synthesis of VII and X-XIV. Compound VII was obtained by the reaction of 6-ethoxycarbonyl-1,2,3,4-tetrahydrocarbazole with iodobenzene at 180-200°C for 6 h in the presence of calcined K_2CO_3, KI, and copper powder. Compounds X-XIV (see Table 1 for data on VII, XI, and XIV) were similarly obtained by the reaction 5-methoxy-1,2,3,4-tetrahydrocarbazole [25] with iodobenzene (18 h, 180-200°C, K_2CO_3 and Cu), 7-methoxy-1,2,3,4-tetrahydrocarbazole [25] with iodobenzene (16 h, 180-200°C, K_2CO_3 and Cu), 1,2,3,4-tetrahydrocarbazole with m-bromoanisole (15 h, 180°C, K_2CO_3 and Cu), 8,9,10,11-tetrahydrobenzo[h]carbazole with iodoben-

* IR spectrum in CS_2 (0.05 M, d 0.4 mm): 830 and 738 cm^{-1} (1,4- and 1,2-disubstituted benzene rings).
† In addition to the comparison of the spectra of XIII and XIV, analysis of the spectra of the model compounds 8,9,10,11-tetrahydrobenz[h]carbazole and 9-phenyl-1,2,3,4-tetrahydrocarbazole facilitated the assignment.

zene (14 h, 170-190°C, K_2CO_3, KI, and Cu), and 1,2,3,4-tetrahydrocarbazole with 2-bromonaphthalene (12 h, 200-210°C, K_2CO_3, KI, and Cu). Compounds X and XII were characterized by means of their PMR spectra, and XIII was characterized by means of its PMR and IR spectra.

Fischer Indolization. These reactions were carried out with 0.5-mmole samples of the hydrazine and ketone. The reaction of the hydrochlorides of I or III with cyclohexanone was carried out by refluxing (for 30 and 60 min, respectively) in 25 and 15% solutions of HCl in absolute alcohol, whereas the reaction of the hydrochloride of II was carried out in absolute alcohol (for 15 min). The reaction mixture was poured into water, and the aqueous mixture was extracted with benzene. The extract was washed with concentrated hydrochloric acid and water, and the organic layer was dried and evaporated thoroughly with a rotary vacuum evaporator to give a mixture of VI and VII (in an overall yield of 89%). Compound VI was isolated in the individual state by crystallization from alcohol. A mixture of XIII and XIV was obtained in 98% overall yield, and XIV was isolated by treatment of the mixture with ether at 20°C. A mixture of X-XII was obtained in 86.5% yield; the mixture was fractionated at 208-210°C (2 mm) and was analyzed for its elementary composition (the results were in agreement with the analysis for XI; see Table 1) and the isomer ratio, which did not change after fractionation.

The reaction of hydrazine IV was carried out in a refluxing alcohol solution of hydrogen chloride with cyclohexanone (15% solution, 10 min) or tetrahydrothiapyrone (10% solution, 45 min). The mixture was poured into water, and the resulting oil was extracted with ether to give VIII in 73.5% yield or IX in 61% yield. UV spectrum of VIII, λ_{max} (log ε): 203 (4.46), 224 (4.49), 264 (4.17), and 305 nm (3.94). Compound XV was similarly obtained in 64% yield from hydrazine V and cyclohexanone (10% HCl in alcohol, 3 min). IR spectrum (in CCl_4): 1738 and 1755 cm^{-1} (d, often observed in the spectra of compounds of the coumarin series). UV spectrum, λ_{max} (log ε): 203 (4.59), 215 (4.64), 276 (4.22), and 320 nm (3.78).

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