6. Ya. P. Stradyn', Khim. Geterotsikl. Soedin., No. 11, 1567 (1979).
7. Ya. P. Stradyn', Khim. Geterotsikl. Soedin., No. 10, 1412 (1981).
8. B. A. Trofimov, A. I. Mikhaleva, A. S. Atavin, E. G. Chebotareva, and M. V. Sigalov, USSR Inventor's Certificate No. 518493; Byull. Izobret., No. 23, 76 (1976).
9. A. I. Mikhaleva, S. E. Korostova, A. N. Vasil'ev, L. N. Balabanova, N. P. Sokol'nikova, and B. A. Trofimov, Khim. Geterotsikl. Soedin., No. 12, 1636 (1977).
10. A. I. Mikhaleva, B. A. Trofimov, and A. N. Vasil'ev, Khim. Geterotsikl. Soedin., No. 2, 197 (1979).

EFFECT OF THE INCLUSION OF A CYCLIC FRAGMENT IN THE CHROMOPHORE ON THE PROPERTIES OF A SPIROPYRAN–MEROCYANINE SYSTEM

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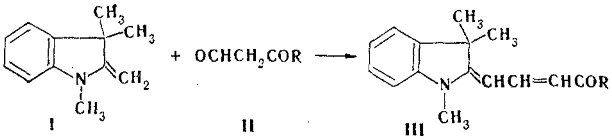
The corresponding merocyanines, which do not display a tendency to form spiropyran structures, are formed in the condensation of 1,3,3-trimethyl-2-methyleneindoline with 5-methyl-2-furoylacetaldehyde, 2-formylcyclohexanone, or 2-formyl-1-tetralone. Spiran compounds in which the spiropyran–merocyanine equilibrium is shifted markedly to favor the closed form are formed when 4a,9-dimethyl-2,3,4,4a-tetrahydrocarbazone — the cyclic analog of the Fischer base — is used in the reaction with salicylaldehydes and benzoylacetaldehydes.

We have previously shown that ω-(2-benzoylvinyl)methyleneindolines (III), which are formed in the reaction of the Fischer base (I) with benzoylacetaldehydes (II, R = aryl), have the properties that are typical for merocyanine structures and do not display a tendency to undergo conversion to the cyclic spiro form [1]. It was subsequently established that the indicated reaction also leads to the corresponding condensation products III (R = 5-methyl-2-furyl), IV, and V in satisfactory yields in the case of carbo- and heterocyclic β-keto aldehydes (5-methyl-2-furoylacetaldehyde, 2-formylcyclohexanone, and 2-formyl-1-tetralone).



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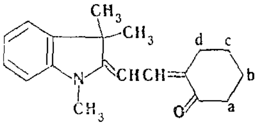

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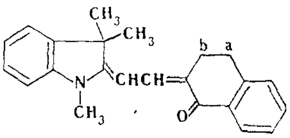

V

With respect to their properties, these merocyanine compounds do not differ fundamentally from the previously described phenyl analogs III (R = aryl) [1]. Their solutions have intense absorption in the visible region and remain unchanged when the temperature is changed or upon irradiation with visible or UV light (Table 1), which indicates the absence of rotation to the closed spiral form. Increased polarity of the medium leads to bathochromic shift (15-22 nm) of the long-wavelength absorption band for merocyanines. A sharp ($\sim$50 nm) hypsochromic blending of the band for compound IV constitutes evidence that the presence

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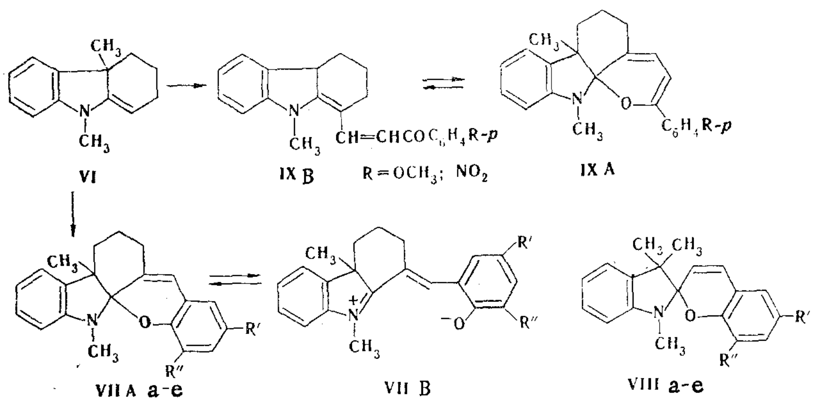
TABLE 1. Characteristics of the Electronic Spectra of Merocyanines

Compound (R)	Toluene		Ethanol	
	λ_{max}, nm	$\varepsilon \cdot 10^{-4}$, liters/mole-cm	λ_{max}, nm	$\varepsilon \cdot 10^{-4}$, liters/mole-cm
III (5-Methyl-2-furyl)	445	5,63	467	4,95
IV	408	3,61	423	4,09
V[a]	453	3,72	474	4,39
IXB (OCH_3)	440	7,33	464	5,84
III ($4\text{-}CH_3OC_6H_4$)[b]	436,5	5,75	455	5,24
IXA (NO_2)	395	1,07	397[в]	1,77
IXB (NO_2)	—	—	520[г]	7,94
III ($4\text{-}NO_2C_6H_4$)[b]	462	3,01	491	3,62

[a] According to the data in [14], λ_{max} 454 nm in benzene and 473 nm in ethanol. [b] According to the data in [1]. [c] Band half-width σ = 3500 cm^{-1}. [d] Band half-width σ = 1580 cm^{-1}.

or absence of additional conjugation systems on the periphery of the chromophore chain of the merocyanine has a substantial effect on the position of the spectral bands. Similar structural effects on the absorption spectra in photomerocyanines of the indole series have been previously observed [2].

Inasmuch as we did not observe a tendency for the merocyanines to undergo conversion to the cyclic spiro form under the influence of the structural factors in the nonindoline fragment of the merocyanine, we studied the possibility of spiro cyclization by the creation of steric hindrance for the open form by the introduction of a cyclic fragment into the chromophore system of the merocyanine in the indoline part of the molecule. With this in mind, we obtained 4a,9-dimethyl-2,3,4,4a-tetrahydrocarbazole (VI) [3] — the cyclic analog of the Fischer base (I).



a $R'=NO_2$, $R''=H$; b $R'=NO_2$, $R''=Br$; c $R'=NO_2$, $R''=OCH_3$; d $R'=R''=NO_2$; e $R'=OCH_3$, $R''=NO_2$

The corresponding spiropyrans VIIAa-e, which, in contrast to their VIII analogs without a saturated cyclic fragment in the chromophore, do not display any signs of photochromic transformations in solutions at room temperature in the process of irradiation with nonpulse UV light sources, are formed smoothly in the condensation of tetrahydrocarbazole VI with substituted nitrosalicylaldehydes. However, under pulse-irradiation conditions spiropyrans VIIAa-d display a tendency to undergo photochromic transformations leading to the formation of the merocyanine forms (VIIB). The spectral-kinetic parameters of these transformations, as compared with the analogous data for VIIIa-c [4], are presented in Table 2. The introduction of a cyclic fragment into the chromophore of the merocyanine gives rise to a bathochromic shift of the long-wave band of photoinduced absorption and, at the same time, dramatically changes the ratio of the stabilities of the spiran and merocyanine forms in series of photochromic compounds: The rate constant for dark decolorization of the photomerocyanines VIIB → VIIA increases by five orders of magnitude.

TABLE 2. Properties of the Photomerocyanines

Compound	Solvent	λ_{max}, nm	k_T, sec^{-1} (20°)
VII a	Hexane	625	$4{,}5 \cdot 10^3$
VII b	Hexane	665	$\sim 3 \cdot 10^{3a}$
VII c	Hexane	645	$2{,}0 \cdot 10^3$
VII d	Toluene	580	$1{,}4 \cdot 10^{-1}$
VIII$_a$^{b}	Toluene	595	$3{,}09 \cdot 10^{-2}$
VIII$_b$^{b}	Toluene	600	$1{,}78 \cdot 10^{-2}$
VIII$_c$^{b}	Toluene	610	$1{,}66 \cdot 10^{-2}$

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[a] A slower component of the dark decolorization process is also observed ($k'_T \approx 5 \cdot 10^2$ sec^{-1}. [b] According to the data in [4].

TABLE 3. Constants for the IXA ⇄ IXB Equilibrium ($R = NO_2$) in Aqueous Alcohol Solutions at 20°C

Alcohol, %	$K = \frac{IXB}{IXA}$
100	0,085
84	0,14
76	0,17
64	0,21
52	0,24

The condensation of tetrahydrocarbazole VI with 4-methoxybenzoylacetaldehyde (II, $R = 4\text{-}CH_3OC_6H_4$) led to IXB ($R = OCH_3$), the spectral properties of which were found to be typical for the open merocyanine form (Table 1): With respect to their order of magnitude, the extinction coefficients resemble the parameters for the merocyanine analog (III, $R = 4\text{-}CH_3OC_6H_4$), whereas the long-wave absorption band, as in the case of spiropyrans VII, was shifted bathochromically as compared with spiropyrans VIII. However, in the condensation of the same base VI with 4-nitrobenzoylacetaldehyde (II, $R = 4\text{-}NO_2C_6H_4$) we obtained a substance, the absorption spectrum of which in toluene differed appreciably from the spectrum of the merocyanine analog (III, $R = NO_2C_6H_4$) (Table 1). Two broad absorption bands, the relative intensities of which changed when the amount of alcohol was varied, were observed in the spectra of solutions of this substance in aqueous alcohol mixtures at 340-600 nm; the spectral curves intersected at the isobestic point. Having assumed that in aqueous alcohol solutions the substance obtained gives an equilibrium mixture of two forms, viz., a cyclic form (with a short-wave absorption band) and a merocyanine form (with a long-wave absorption band), that the spectral parameters of each form do not undergo substantial deviations when the amount of alcohol is changed, and that the absorption band of each form has the form of a Gaussian curve [5]

$$D = D_{\max} \cdot e^{-\frac{(\nu - \nu_{\max})^2}{\sigma^2} \cdot \ln 2},$$

we determined the parameters of the individual absorption bands, viz., the amplitude (D_{max}), the position of the center of the band (ν_{max}), and the half-width (σ) for each spectral curve; the ν_{max} and σ values for each band for all of the spectral curves were assumed to be identical. Considering the fact that the relationship between the amplitudes of the absorption bands of the cyclic and merocyanine forms $D_{max}A$ and $D_{max}B$, their extinction coefficients ε_A and ε_B, the starting concentration of the solution c_0, and the cuvette thickness l is expressed by linear regression equation

$$D_{\max}{}^{A} = c_0 l \varepsilon_A - \frac{\varepsilon_A}{\varepsilon_B} D_{\max}{}^{B},$$

on the basis of the $D_{max}A = f(D_{max}B)$ dependence obtained we determined the ε_A and ε_B values (Table 1). The values obtained for the short-wave band were close to the data for a solution in toluene, while those obtained for the long-wave band were close to the data for merocyanine analog III ($R = 4\text{-}NO_2C_6H_4$). The data obtained constitute unambiguous evidence that in aqueous alcohol solutions IX ($R = NO_2$) is an equilibrium mixture of the cyclic spiran (IXA) and merocyanine (IXB) forms; as in the case of indoline spiropyrans [6], the equilibrium is shifted to favor the merocyanine form as the polarity of the medium is increased. The parameters of the equilibrium for aqueous alcohol mixtures with various compositions are presented in Table 3.

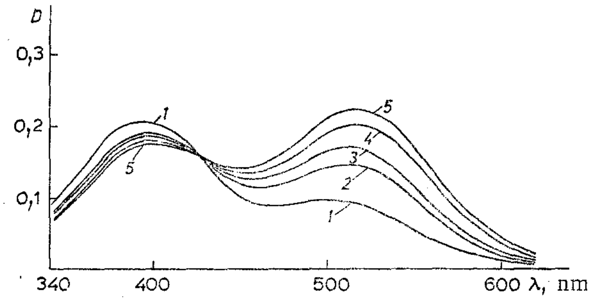

Fig. 1. Absorption spectra of IX (R = NO_2) in aqueous alcohol mixtures with various amounts of alcohol: 1) 100%; 2) 84%; 3) 76%; 4) 64%; 5) 52% (c_0 = $1.25 \cdot 10^{-5}$ mole/liter).

The data from the electronic spectra are also confirmed by the PMR spectra, from an analysis of which it follows that 90% of IX with R = NO_2 exists in the closed form in C_6D_6, as compared with ∿3/4 in $CDCl_3$, whereas the percentage of the spiran form of IX with R = OCH_3 in $CDCl_3$ amounts to only slightly more than 10%. These conclusions are based on the fact that the ratios of the intensities of the singlet signals of the N-methyl group for the spiran (δ ∿ 2.7 ppm) and merocyanine (δ ∿ 3.6 ppm) forms for the cases indicated above are respectively, 9:1, 3:1, and 1:7. In addition, in the merocyanine structure the exocyclic protons are trans-oriented, whereas in the spiropyran structure the same protons (4' and 5') should be cis-oriented relative to one another. The change in the spin-spin coupling constants (SSCC) confirms this graphically: J is on the order of 14 Hz (trans) for the merocyanine forms, whereas J ≈ 6 Hz (cis) for the spiran forms.

Thus on the basis of the data obtained in the present research it may be concluded that steric factors, particularly the introduction of a cyclic fragment into the chromophore chain, may have a decisive effect on the change in the relative stabilities of the spiran and merocyanine forms of spiropyrans, although the electronic character of the substituents also plays a fairly large role.

In a paper by V. I. Minkin and co-workers [7] on the basis of the results of quantum-chemical calculations it was shown that 1,3,3-trimethylindolinespiro-2,2'-[2H]-pyrans should exist in the form of open merocyanine structures, which is not justified for IX (R = NO_2). In certain extreme cases allowance for the electronic and steric effects of the substituents, as well as the effect of the medium, evidently may lead to more nearly complete agreement between the results of the theoretical calculations and the experimental data.

EXPERIMENTAL

The electronic absorption spectra of solutions of the merocyanines were recorded with VSU-2P and SF-8 spectrophotometers. The spectral curves were broken down into a combination of two Gaussian bands by the method in [8]. The behavior of the spiropyrans under pulse-irradiation conditions was studied as described in [9]. The PMR spectra were recorded with a Varian CFT-20 high-resolution NMR spectrometer with an operating frequency of 80 MHz with tetramethylsilane as the internal standard. The course of the reactions and the purity of the products were monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates.

1,3,3-Trimethyl-2-[3-(5-methyl-2-furoyl)-2-propen-1-ylidene]indoline (III, R = 5-methyl-2-furyl). Formylation of 2-acetyl-5-methylfuran by the method in [10] gave the sodium salt of (5-methyl-2-furoyl)acetaldehyde (the crude product had mp 245-248°C). A 1-g sample of this salt was dissolved in water, and the solution was acidified carefully with 5% hydrochloric acid and extracted rapidly with ether. The ether solution was washed with water and dried, the ether was removed by distillation, and the resulting aldehyde [0.87 g (5.8 mmole)] was dissolved in 10 ml of absolute ethanol. A solution of 0.97 g (5.6 mmole) of Fischer base I in 10 ml of absolute alcohol was added to the solution, and the mixture was refluxed for 2 h. It was then poured into a beaker and allowed to stand overnight. The resulting crystalline mass was chromatographed on Al_2O_3 with elution of the product with acetone–petroleum ether (1:8). The solvent was removed by distillation, and the residue was crystallized twice from alcohol to give red crystals with R_f 0.18 [acetone–petroleum ether (1:8)]. PMR spectrum

TABLE 4. Merocyanines and Spiropyrans

Compound (R)	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
III (5-methyl-2-furyl)	148—149	79,1	7,1	4,6	$C_{20}H_{21}NO_2$	78,2	6,9	4,6	42
IV	164—165	81,1	8,3	4,9	$C_{19}H_{23}NO$	81,1	8,2	5,0	40
V	211—212[a]	84,4	7,3	4,3	$C_{23}H_{23}NO$	83,9	7,0	4,3	64
VII a	149	72,4	6,0	7,9	$C_{21}H_{20}N_2O_3$	72,4	5,8	8,0	40
VII b	198	59,3	4,5	6,8	$C_{21}H_{19}BrN_2O_3$	59,0	4,5	6,6	44
VII c	188	69,9	5,4	7,3	$C_{22}H_{22}N_2O_4$	69,8	5,9	7,4	36
VII d	220—221	64,1	4,9	10,7	$C_{21}H_{19}N_3O_5$	64,2	5,1	10,3	73
VII e	207—209	69,5	5,7	7,2	$C_{22}H_{22}N_2O_4$	69,8	5,9	7,4	57
IX (NO_2)	169—171	73,3	6,2	7,4	$C_{23}H_{22}N_2O_3$	73,8	6,0	7,5	34
IX (OCH_3)	176—178	80,5	7,0	3,9	$C_{24}H_{25}NO_2$	80,2	7,0	3,9	28

[a] This compound had mp 206-207 °C [14].

($CCl_4 + C_6D_{12}$): 1.66 (s, 3-CH_3), 2.36 (s, furan ring 5-CH_3), 3.17 (s, 1-CH_3), 5.44 (d, $J_{1',2'}$ = 12.7 Hz, 1-H), 7.94 (q, $J_{1',2'}$ = 12.7; $J_{2',3'}$ = 14.2 Hz, 2'-H), 6.50 (d, $J_{2',3'}$= 14.2 Hz, 3'-H), 6.90 (d, J = 2.8 Hz, furan ring 3-H), 6.01 (d, J = 2.8 Hz, furan ring 4-H), and 6.67-7.13 (m) ppm.

1-(1,3,3-Trimethyl-2-indolinylidene)-2-(2-oxocyclohexylidene)ethane (IV). A 0.45 g (3.57 mmole) sample of the aldehyde was obtained from 1 g of the sodium salt of 2-oxo-1-formylcyclohexane (obtained by formylation of cyclohexanone [11]) by the method described above and was dissolved in 10 ml of absolute ethanol. A solution of 0.62 g (3.57 mmole) of indoline I in 5 ml of alcohol was added to this solution, and the mixture was allowed to stand for 3 days. It was then evaporated to half its original volume, and the crystalline precipitate was chromatographed with a column filled with Al_2O_3 by elution with acetone—heptane (1:4). The solvent was removed by distillation, and the residue was crystallized from alcohol to give yellow crystals with R_f 0.43 [acetone—heptane (1:4)]. PMR spectrum (CD_3COCD_3): 1.57 (s, 3'-CH_3), 1.6-1.9 (m, $H_{b,c}$), 2.2-2.6 (m, $H_{a,d}$), 3.26 (s, 1'-CH_3), 5.35 (d, J = 13.3 Hz, 1-H), 7.90 (d, J = 13.3 Hz, 2-H), and 6.8-7.3 (m) ppm.

1-(1,3,3-Trimethyl-2-indolinylidene)-2-(1-oxo-1,2,3,4-tetrahydro-2-naphthylidene)-ethane (V). The sodium salt of 1,2,3,4-tetrahydro-1-oxo-2-naphthaldehyde was obtained by formylation of 1-tetralone by the method in [10] and was converted to the copper salt (the crude copper salt melted with decomposition at 216-218°C). The free aldehyde [0.67 g (3.85 mmole)] was obtained from 1 g of this salt by the usual method [1] and dissolved in 15 ml of absolute alcohol, and 0.67 g (3.85 mmole) of the Fischer base was added to the solution. After 3 days, the precipitated crystals were removed by filtration and crystallized twice from alcohol to give shiny, violet, acicular crystals. PMR spectrum (CD_3COCD_3): 1.65 (s, 3'-CH_3), 1.7-1.8 (m, H_a), 2.3-2.4 (m, H_b), 3.31 (s, 1'-CH_3), 5.61 (d, J = 13.3 Hz, 1-H), 8.17 (d, J = 13.3 Hz, 2-H), and 6.8-7.4 (m) ppm.

4a,9-Dimethyl-1,2,3,4-tetrahydro-4aH-carbazolium Iodide. The hydrazone was obtained from 78.4 g (0.725 mole) of phenylhydrazine and 85.7 g (0.765 mole) of 2-methylcyclohexanone [12] and was converted by cyclization in glacial acetic acid [3] to 4a-methyl-1,2,3,4-tetrahydro-4aH-carbazole, which gave the methiodide when it was refluxed in 100 ml (1.6 mole) of CH_3I for 30 min. The reaction product was crystallized four times from alcohol to give yellowish crystals with mp 213-214°C (mp 211°C [13]).

1,3-Dimethyl-6'-nitro-3,3'-trimethylenespiro(indoline-2,2'-2H-chromene) (VIIa). Treatment of 4a,9-dimethyl-1,2,3,4-tetrahydro-4aH-carbazolium iodide with a 10% solution of NaOH gave 1.6 g (8 mmole) of free base VI, which was dissolved in 5 ml of absolute alcohol and added dropwise to a solution of 1.38 g (8.5 mmole) of 5-nitrosalicylaldehyde in 30 ml of absolute alcohol. The mixture was heated on a water bath for 40 min, after which the alcohol was removed by distillation to two-thirds of the original volume, and the precipitated light-yellow crystals were crystallized from alcohol.

1,3-Dimethyl-6'-nitro-8'-bromo-3,3'-trimethylenespiro(indoline-2,2'-2H-chromene) (VIIb). This compound was obtained from 1.6 g (8 mmole) of base VI and 2.09 g (8.5 mmole) of 3-bromo-5-nitrosalicylaldehyde by a method similar to that used to prepare VIIa. The yellow crystals that formed immediately were recrystallized from acetone.

1,3-Dimethyl-6'-nitro-8'-methoxy-3,3'-trimethylenespiro(indoline-2,2'-2H-chromene) (VIIc). This compound was obtained from 1.6 g (8 mmole) of base VI and 1.58 g (8.5 mmole) of 3-methoxy-5-nitrosalicylaldehyde by a method similar to that used to prepare VIIa. Yellow crystals were isolated after recrystallization from alcohol.

1,3-Dimethyl-6',8'-dinitro-3,3'-trimethylenespiro(indoline-2,2'-2H-chromene) (VIId). The condensation of 0.25 g (1.17 mmole) of 3,5-dinitrosalicylaldehyde in 10 ml of alcohol and of 0.23 g (1.16 mmole) of base VI in 5 ml of alcohol was carried out under the conditions described above. Light, shiny, yellow plates of the spiropyran were obtained after recrystallization from alcohol.

1,3-Dimethyl-6'-methoxy-8'-nitro-3,3'-trimethylenespiro(indoline-2,2'-2H-chromene) (VIIe). This compound was obtained under the conditions indicated above from 0.22 g (1.1 mmole) of base VI and 0.23 g (1.15 mmole) of 3-nitro-5-methoxysalicylaldehyde. The product was crystallized from alcohol and was isolated in the form of fine yellow crystals.

1-[2-(p-Nitrobenzoyl)vinyl]-4a,9-dimethyl-2,3,4,4a-tetrahydrocarbazole (IX, R = NO_2). A solution of 0.55 g (2.86 mmole) of p-nitrobenzoylacetaldehyde [1] in 40 ml of alcohol was added to a solution of 0.57 g (2.86 mmole) of base VI in 5 ml of absolute ethanol, and the mixture was refluxed with calcined $MgSO_4$ for 2 h, after which it was poured into a beaker. The solvent was evaporated and the resinous precipitate was chromatographed on Al_2O_3 by elution with acetone—petroleum ether (1:8). The solvent was removed by distillation, and the product was recrystallized from alcohol to give orange light crystals with R_f 0.58 [acetone—petroleum ether (1:3)].

1-[2-(p-Methoxybenzoyl)vinyl]-4a,9-dimethyl-2,3,4,4a-tetrahydrocarbazole (IX, R = OCH_3). A solution of 0.85 g (4.27 mmole) of base VI and 0.76 g (4.27 mmole) of p-methoxybenzoylacetaldehyde [1] in 20 ml of absolute alcohol was refluxed with $MgSO_4$ for 2.5 h, after which it was poured into a beaker, and the alcohol was allowed to evaporate. The resinous precipitate was purified chromatographically by the method described above. Fine yellow crystals with R_f 0.55 [acetone—petroleum ether (1:3)] were obtained after recrystallization from alcohol.

LITERATURE CITED

1. A. P. Sidorov, M. A. Gal'bershtam, and N. M. Przhiyalgovskaya, Khim. Geterotsikl. Soedin., No. 2, 202 (1981).
2. E. V. Braude and M. A. Gal'bershtam, Khim. Geterotsikl. Soedin., No. 2, 207 (1979).
3. K. H. Pausacker, J. Chem. Soc., No. 2, 621 (1950).
4. M. A. Gal'bershtam, N. M. Przhiyalgovskaya, O. R. Khrolova, I. V. Manakova, G. K. Bobyleva, and N. N. Suvorov, Khim. Geterotsikl. Soedin., No. 8, 1069 (1977).
5. V. M. Vdovenko, editor, Spectroscopic Methods in the Chemistry of Complexes [in Russian], Khimiya, Moscow—Leningrad (1964), pp. 6, 102.
6. R. S. Bertelson, in: Photochromism, G. Brown, ed., Interscience, New York (1971), p. 171.
7. B. Ya. Simkin, V. I. Minkin, and L. E. Nivorozhkin, Khim. Geterotsikl. Soedin., No. 9, 1180 (1978).
8. M. A. Gal'bershtam, E. M. Bondarenko, O. R. Khrolova, G. K. Bobyleva, Yu. B. Pod'yachev, N. M. Przhiyalgovskaya, and N. N. Suvorov, Khim. Geterotsikl. Soedin., No. 12, 1654 (1979).
9. Yu. P. Strokach, V. F. Mandzhikov, and V. A. Barachevskii, Opt. Spektrosk., 48, 402 (1980).
10. E. Benary, Chem. Ber., 61, 2253 (1928).
11. Organic Syntheses [Russian translation], Collective Vol. 11, Inostr. Lit., Moscow (1961), p. 27.
12. H. C. Brown and C. P. Garg, J. Am. Chem. Soc., 83, 2952 (1961).
13. G. Plancher, Atti Linc., Ser. 5, 9, No. 1, 220 (1900).
14. Yu. L. Slominskii and I. D. Radchenko, Ukr. Khim. Zh., No. 5, 546 (1974).