POLYMETHINE DYES WITH SEVERAL CONJUGATED CHROMOPHORES

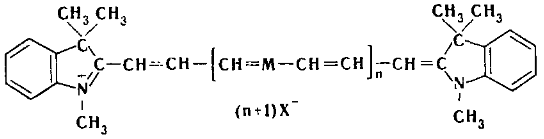
F. A. Mikhailenko, G. G. Dyadyusha,
and A. N. Boguslavskaya

UDC 541.651:547.759'789.67

Triscyanine dyes with three successively conjugated chromophores were obtained from diquaternary salts of four isomeric dimethylbenzobisthiazoles and two isomeric hexamethylbenzodipyrrolenines. The spectra of the dyes contain three absorption bands, the intensities of which depend on the angles formed by the directions of the interacting chromophores and are determined by the structure of the heteroring. The magnitude of the separation of the frequencies of the two extreme absorption maxima of the triscyanines exceeds the magnitude of the separation of the frequencies of the maxima of the corresponding biscyanine dyes by a factor of $\sqrt{2}$. A dye with four successively conjugated chromophores was obtained from centrosymmetric hexamethylbenzodipyrrolenine, and its absorption spectrum was examined.

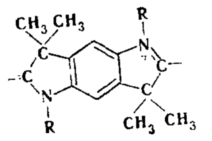
The interaction of bonded chromophores has been investigated primarily in the case of dye molecules with two chromophores [1]. The most distinct results were obtained for biscyanine dyes from isomeric benzobisthiazoles and benzodipyrrolenines [2, 3]. These dyes are distinguished by the rather pronounced interaction of the chromophores and by the rigid and unambiguous* structure of the molecule, and they consequently have narrow distinct absorption bands. In studying the peculiarities of the absorption spectra of compounds with three or more chromophores we became interested in dyes with these same nuclei.

The synthesis of triscyanine I from centrosymmetric benzodipyrrolenine was described in [5]. Using a similar method we obtained dye II from linear m-benzodipyrrolenine and triscyanines III-VI from four isomers of benzobisthiazole. In addition, we were able to obtain tetrakiscyanine VII with four successively conjugated chromophores bonded by centrosymmetric benzodipyrrolenine rings.

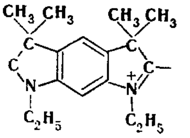


I–VII

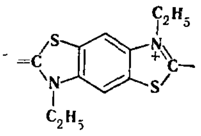
I $n=2$, X=CH_3SO_4, M=M_1, R=CH_3; II $n=2$, X=ClO_4, M=M_2; III $n=2$, X=ClO_4, M=M_3; IV $n=2$, X=ClO_4, M=M_4; V $n=2$, X=I, M=M_5; VI $n=2$, X=ClO_4, M=M_6; VII $n=3$, X=Br, M=M_1, R=C_2H_5



M_1



M_2

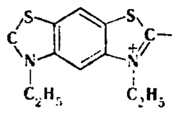


M_3

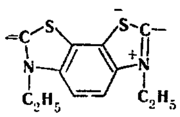
---

*The trimethine chain of carbocyanines that does not contain substituents has an all-trans orientation [4].

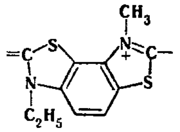
Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 370-376, March, 1975. Original article submitted February 5, 1974.



M₄



M₅

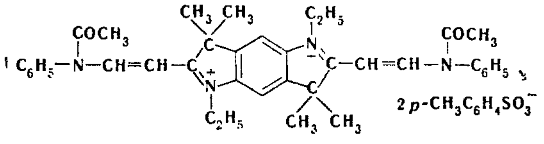


M₆*

---

*Thiazole rings with an ethyl group attached to the nitrogen atoms form the extreme chromophores.

The synthesis of dye VII was accomplished in the same way as the synthesis of the triscyanines, but diethoxymethyl acetate VIII was replaced by bisacetanilidovinyl derivative IX in the second step.



IX

In order to increase the solubilities of dyes VII and II-VI, ethyl groups were substituted for methyl groups at the nitrogen atoms (in contrast to dye I).

In the case of dye VI, the usual method for the synthesis of triscyanines gave a mixture of isomers, inasmuch as the thiazole rings of this heterocycle are not equivalent. In order to synthesize the isomer of interest to us, we therefore alkylated 2,7-dimethylbenzo[1,2-d:3,4-d']bisthiazole with ethyl p-toluenesulfonate (X) at the nitrogen atom in the 3 position [6], the mono salt was condensed with 1,3,3-trimethyl-2-formylmethyleneindoline XI to give the mono dye, which was alkylated with methyl o-nitrobenzenesulfonate (XII) at the nitrogen atom in the 8 position, and the resulting salt reacted with VIII to give dye VI.

The spectral characteristics of nitromethane solutions of dyes I-VII were compared with the data for the corresponding biscyanines (see Table 1).

Inasmuch as the interaction of two conjugated chromophores gives two absorption bands [7], it was natural to assume that the interaction of three chromophores would result in the formation of three absorption bands. As in the case of the cyanine dyes, the intensities of the absorption bands should depend on the directions of the interacting chromophores. However, only two electron-vibrational absorption bands are observed in most cases in the absorption spectra of the triscyanines. All of the triscyanines that we studied have an axis of symmetry but no inversion center, and it is therefore unnecessary to expect strict prohibition of one of the absorption bands. From the point of view of a model of the interaction of three equivalent oscillators, in which the extreme ones are symmetrical, the middle absorption band corresponds to excitation of the symmetrical vibrations of the extreme oscillators, whereas the middle oscillator is not excited (Fig. 1). The frequency of such vibrations should approach the frequency of the isolated extreme chromophore, i.e., this band should be close to the corresponding absorption band of the parent monodye. The extreme chromophores participate to a lesser extent in the two other absorption bands. The long-wave band should correspond to the synphase vibration of all three chromophores and have the maximum intensity when the chromophores are linearly oriented (Fig. 1a). In the case of the short-wave band, the vibrations of the electrons of the extreme chromophores are opposite with respect to their phase to the vibrations of the electrons of the middle chromophore. The intensity of this absorption band should therefore initially decrease as the angle between the chromophore decreases with retention of the axis of symmetry (Fig. 1b). If the angles between the chromophores reach 90°, the molecule takes on a π-shaped form — the extreme chromophores cease making contributions to the intensity of the long-wave and short-wave absorption bands (Fig. 1c); only the intensity due to the middle chromophore is divided between these bands. In this case the middle absorption band should be very intense.

In fact, the absorption spectra of isomeric triscyanines III-V (Fig. 2) differ markedly with respect to the character of the intensity distribution. The absorption bands with chief maxima at 699, 495 (Fig. 3), 700, and 496 nm that are distinctly observed in the spectra

TABLE 1. Spectral Characteristics of Dyes I-VII and of the Corresponding Biscyanines

Compound	Dyes I-VII				Biscyanines [2,3,14,15]			
	λ_{max}, nm ($\varepsilon \cdot 10^{-5}$)			$\Delta_{(1-3)}\nu_{max}$, cm⁻¹	λ_{max}, nm		$\Delta_{(1-2)}\nu_{max}$, cm⁻¹	$\frac{\Delta_{(1-3)}\nu_{max}}{\Delta_{(1-2)}\nu_{max}}$
	1	2	3		1	2		
I	495 (0,40)	560 —	699 (4,40)	5890	507	646	4240	1,39
II	—	538 (1,30)	620 (4,20)	—	515	592	2530	—
III	496 (0,50)	562 (0,35)	700 (6,50)	5870	504	638	4160	1,41
IV	506 —	560 (1,30)	685 (4,92)	5160	510	631	3760	1,37
V	501 —	553 (3,08)	673 (1,28)	5100	506	621	3660	1,39
VI	—	541 (1,88)	624 (3,80)	—	512	594	2700	—
VII	529 (0,80)	—	729 (5,52)	5180	507	646	4240	1,22

of similarly-constructed dyes I and III should be assigned to the first and third electron transitions of the triscyanine. This is attested to by the fact that these maxima are found on the long-wave and short-wave sides of the long-wave and short-wave maxima of the corresponding biscyanines (Fig. 3 and Table 1). In the case of three equivalent chromophores, if one assumes that only the adjacent chromophores interact and their interaction is the same as in the case of biscyanines, the splitting of these bands [$\Delta_{(1-3)}\nu_{max}$] should have exceeded the splitting of the frequency for biscyanines [8] by a factor of $\sqrt{2}$. As seen from the last column in Table 1, this assumption is justified. The side maxima on the short-wave slopes of the absorption curves are apparently due to the vibrational structure [9]. However, the maxima at 560 and 562 nm, respectively, for I and III, which do not fit into the normal vibrational series, are possibly related to the second transition. Formally speaking, these transitions are not forbidden by the selection rules because of the absence of an inversion center. Their low intensities can be explained by a close-to-linear orientation of the chromophores (Fig. 1a). This structure is even more likely for triscyanines I and III than for the corresponding biscyanines, the molecules of which are centrosymmetric, and the angle between the directions of the chromophores is 180° [7]. In the spectrum of dye I there is an individual electron transition at 560 nm, which follows from the circular dichroism spectrum of the complex of this dye with DNA [10].

The two distinct absorption bands in the spectra of dyes II, IV (Fig. 2) and VI cannot be assigned to the first and third transitions. In fact, a comparison with the spectra of biscyanines showed that the short-wave band of these dyes lies between the absorption bands of biscyanines (Table 1). Its position is close to the position of the absorption band of the parent monocyanine. This band should therefore be assigned to the second electron-vibrational transition. The weak band in the shorter-wave region (506 nm) observed in the spectrum of dye IV, the distance of which from the long-wave band corresponds satisfactorily to the expected splitting of the frequencies of the triscyanine as compared with the biscyanine, may serve as a confirmation of this assignment. The low intensity of the short-wave band in the spectra of these dyes can be explained by assuming obtuse angles between the chromophores (Fig. 1b). In fact, the ratio of the intensities of the absorption bands of the corresponding biscyanines suggests angles of 150° for dye IV and 120° for VI [7], and the extinction of the middle maximum of triscyanine VI with a greater acute angle between the chromophores is greater than for isomer IV. It should be noted that the shifts of the long-wave band of the triscyanine from the long-wave band of the corresponding biscyanine are 28 and 30 nm in the spectra of dyes II and VI as compared with 52-62 nm for dyes I and III-V. In precisely the same way, the interaction of the chromophores of biscyanines corresponding to dyes II and VI is less than the observed in the case of I and III-V.

At first glance, the absorption spectrum of triscyanine V (Fig. 2), the most intense maximum of which remains virtually unshifted as compared with the absorption maximum of the simple thiacarbocyanine, seems to be the most surprising spectrum. On the basis of our theoretical concepts, it should be interpreted as a second maximum, inasmuch as a distinct

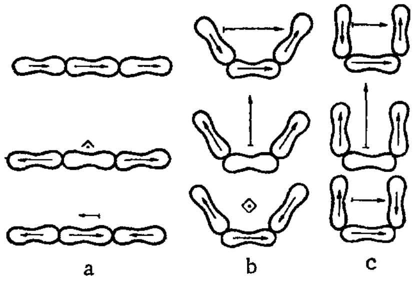


Fig. 1

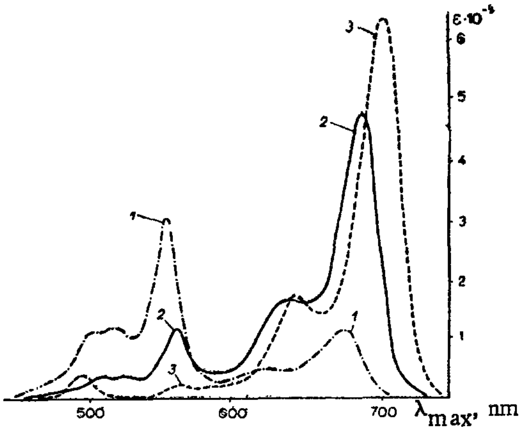


Fig. 2

Fig. 1. Vibrations of the electrons in a system of three-bonded chromophores: a) when they are linearly oriented; b) when there is an obtuse angle between them; c) when there is a right angle between them. The energies of the transition increase from the top to the bottom. The resulting dipole moments of the transitions are indicated by arrows above the diagrams.

Fig. 2. Absorption curves of dyes III-V in nitromethane: 1) dye V; 2) dye IV; 3) dye III.

absorption band of lower intensity is observed in the long-wave portion of the spectrum of this dye, and there is an obvious anomaly in the vibrational structure with a maximum at 501 nm on the short-wave slope of the second absorption band. The theoretical ratio of the splittings of the frequencies of the triscyanine and biscyanine is well satisfied here also (Table 1). The absorption spectrum of this dye therefore is in complete agreement with the theoretically-expected absorption for the π-shaped triscyanine with angles of ~90° between the chromophores. In fact, the ratio of the intensities in the spectrum of the corresponding biscyanine show that the angle between the chromophores in it is close to 90° [7].

One should have expected the appearance of four absorption bands in the absorption spectrum of tetrakiscyanines, and the extreme bands should be even more separated than in the spectrum of the corresponding triscyanine. When allowance is made for the interaction of only the nearest neighbors in dyes with many successively-connected chromophores, the extreme bands should be separated as the number of chromophores increases but by a factor of no more than two as compared with the corresponding biscyanine dyes [8]. Moreover, the absorption bands of a dye with (n = 1) chromophores should be located between the absorption bands of a dye with n chromophores, and for a symmetrical compound the odd bands, beginning with the long-wave edge, should correspond to asymmetrical transitions, whereas the even bands should correspond to symmetrical transitions [11]. Only two distinct absorption bands are observed in the absorption spectrum of the investigated tetrakiscyanine VII (Fig. 3). The first and most intense band, as one should have expected, is shifted bathochromically as compared with the long-wave band of triscyanine I. The second band cannot be considered to be the extreme short-wave band because the splitting in the spectrum of this dye is less than that in the spectrum of triscyanine I (Table 1). Inasmuch as this band is situated between the second and third bands of the triscyanine, it should be assigned to the third transition. Odd-numbered transitions are not observed in the tetrakiscyanine molecule VII, inasmuch as its molecule should have an inversion center, and such transitions are prohibited by the selection rules [12].

The conjugation of three or four chromophores in the investigated compounds is also confirmed by the fact that bands characteristic for the corresponding biscyanines and the parent monocyanines [13] appear in the spectra when solutions of these dyes are partially decolorized with acid or base.

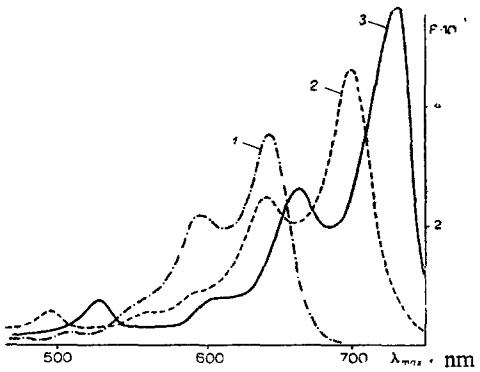


Fig. 3. Absorption curves of triscyanine I, tetrakiscyanine VII, and the corresponding biscyanine in nitromethane: 1) biscyanine; 2) triscyanine I; 3) tetrakiscyanine VII.

EXPERIMENTAL

Dyes II-V. A 5-ml sample (1.2 g in the case of II) of acetic anhydride was added to a refluxing solution of 2 mmole of the bisethyltosylates of 3,5-dihydro-2,3,3,5,5,6-hexamethylbenzo[1,2-b:5,4-b']dipyrrole (dye II), 2,6-dimethylbenzo[1,2-d:4,5-d']bisthiazole (dye III), 2,6-dimethylbenzo[1,2-d:5,4-d']bisthiazole (dye IV) and 2,7-dimethylbenzo[1,2-d:4,3-d']bisthiazole (dye V), obtained by heating the appropriate bases with excess X at 150° for 1 h, and 0.4 g (2 mmole) of XI in 20 ml of acetic acid, after which the mixture was refluxed for 10 min. The solvents were vacuum evaporated until the volume of the solution was two thirds of the original volume, 4 ml of VIII and 5 ml of pyridine were added to the residue, and the solution was refluxed for 30 min. The solvents were vacuum evaporated to dryness, and the residue was washed with ether, dissolved in chloroform, and chromatographed with a column filled with aluminum oxide, with elution initially with chloroform and then with chloroform containing 10% methanol. In the case of dyes V and VI, acetic acid was passed through the column containing aluminum oxide, and the dyes were chromatographed with pure chloroform. The anion was exchanged in methanol solution for the perchlorate ion (dyes II-IV and VI) or the iodide ion (dye V), and the products were crystallized twice.

2-[3-[3,5-Dihydro-3,3,5,5-tetramethyl-1,7-diethyl-6-[3-(1,3,3-trimethyl-2-indolinylidene)propenyl]benzo[1,2-b:5,4-b']dipyrrolium-2(1H)ylidene]propenyl]-3,5-dihydro-3,3,5,5-tetramethyl-1,7-diethyl-6-[3-(1,3,3-trimethyl-2-indolinylidene)propenyl]benzo[1,2-b:5,4-b']-dipyrrolium Triperchlorate (II). This compound, with mp 250° (dec., from methanol), was obtained in 14% yield. Found: Cl 8.1; N 7.0%. $C_{67}H_{83}Cl_3N_6O_{12}$. Calculated: Cl 8.3; N 6.6%.

2-[3-[3,7-Diethyl-6-[3-(1,3,3-trimethyl-2-indolinylidene)propenyl]benzo[1,2-d:4,5-d']-bisthiazolium-2(3H)ylidene]propenyl]-3,7-diethyl-6-[3-(1,3,3-trimethyl-2-indolinylidene)-propenyl]benzo[1,2-d:4,5-d']bisthiazolium Triperchlorate (III). This compound, with mp >300° (dec., from nitromethane), was obtained in 9% yield. Found: Cl 8.4; S 10.4%. $C_{55}H_{59}Cl_3N_6O_{12}S_4$. Calculated: Cl 8.6; S 10.4%.

2-[3-[3,5-Diethyl-6-[3-(1,3,3-trimethyl-2-indolinylidene)propenyl]benzo-[1,2-d:5,4-d']-bisthiazolium-2(3H)ylidene]propenyl]-3,5-diethyl-6-[3-(1,3,3-trimethyl-2-indolinylidene)-propenyl]benzo[1,2-d:5,4-d']bisthiazolium Triperchlorate (IV). This compound, with mp >300° (dec., from nitromethane), was obtained in 10% yield. Found: Cl 8.5; S 10.6%. $C_{55}H_{59}Cl_3N_6O_{12}S_4$. Calculated: Cl 8.6; S 10.4%.

2-[3-[3,6-Diethyl-7-[3-(1,3,3-trimethyl-2-indolinylidene)propenyl]benzo-[1,2-d:4,3-d']-bisthiazolium-2(3H)ylidene]propenyl]-3,6-diethyl-7-[3-(1,3,3-trimethyl-2-indolinylidene)-propenyl]benzo[1,2-d:4,3-d']bisthiazolium Triiodide (V). This compound, with mp 237° (dec., from methanol containing sodium iodide), was obtained in 8% yield. Found: I 29.5; S 9.8%. $C_{55}H_{59}I_3N_6S_4$. Calculated: I 29.0; S 9.7%.

7-[3-[8-Methyl-3-ethyl-2-[3-(1,3,3-trimethyl-2-indolinylidene)propenyl]benzo[1,2-d:-3,4-d']bisthiazolium-7(8H)ylidene]propenyl]-8-methyl-3-ethyl-2-[3-(1,3,3-trimethyl-2-indolinylidene)propenyl]benzo[1,2-d:3,4-d']bisthiazolium Triperchlorate (VI). A solution of 0.65 g (1.5 mmole) of 2,7-dimethyl-3-ethylbenzo[1,2-d:3,4-d']bisthiazolium p-toluenesulfonate, obtained by heating the base with excess X at 130° for 30 min, and 0.6 g (3 mmole) of XI in 15 ml of acetic anhydride were refluxed for 10 min, after which the mixture was vacuum evaporated to dryness and the residue was washed several times with dry ether. A 0.85-g (4 mmole) sample of XII was added to the residue, and the mixture was heated at 120° (in a bath) for 1 h. The melt was washed with dry ether, after which 3 ml of VIII, 10 ml of pyridine, and 2 ml of acetic anhydride were added, and the mixture was refluxed for 30 min. The dye was purified by the method used to purify dyes II-V to give a product with mp >300° [dec., from nitromethane-methanol (1:2)] in 9% yield. Found: Cl 8.9; S 10.7%. $C_{53}H_{55}Cl_3N_6O_{12}S_4$. Calculated: Cl 8.8; S 10.7%.

3,7-Dihydro-3,3,7,7-tetramethyl-1,5-diethyl-2,6-bis(acetanilidovinyl)benzo[1,2-b:4,5-b']dipyrrolium Di(p-toluenesulfonate) (IX). A solution of 3.2 g (5 mmole) of the bisethyltosylate of centrosymmetric hexamethylbenzodipyrrolenine XIII, obtained by the method used to prepare the diquaternary salt for dyes II-V, and 2.2 g (10.1 mmole) of diphenylformamidine in 120 ml of acetic anhydride were refluxed for 20 min, after which the mixture was vacuum evaporated to dryness, and the residue was washed successively with ether and twice with acetone to give 2.65 g (57%) of a product with mp 234° (dec.). Found: S 7.1%. $C_{52}H_{58}N_4O_8S_2$. Calculated: S 6.9%.

2,6-Bis[3-[3,7-dihydro-3,3,7,7-tetramethyl-1,5-diethyl-6-[3-(1,3,3-trimethyl-2-indolinylidene)propenyl]benzo[1,2-b:4,5-b']dipyrrolium-2(1H)ylidene]propenyl]-3,7-dihydro-3,3,7,7-tetramethyl-1,5-diethylbenzo[1,2-b:4,5-b']dipyrrolium Tetrabromide (VII). A 6-ml sample of acetic anhydride was added to a refluxing solution of 1.92 g (3 mmole) of XIII and 0.6 g (3 mmole) of XI in 48 ml of acetic acid, after which the mixture was refluxed for 10 min and vacuum evaporated to dryness. A 0.93-g (1 mmole) sample of IX, 1 g of anhydrous sodium acetate, and 60 ml of acetic anhydride were added to the residue, and the mixture was refluxed for 15 min. It was then vacuum evaporated to dryness, and the residue was extracted with 100 ml of boiling chloroform. The chloroform solution was evaporated to dryness, and the readily soluble impurities were extracted from the residue by washing with acetone. The residue, which, according to its absorption curve, was almost pure VII, was chromatographed on aluminum oxide with chloroform-methanol (4:1). The dye was converted to the bromide in methanol solution by the action of tetramethylammonium bromide. Two crystallizations from methanol gave 0.17 g (10%) of a product with mp >300° (dec.). Found: Br 19.5; N 7.1%. $C_{88}H_{110}Br_4N_8$. Calculated: Br 20.0; N 7.1%.

LITERATURE CITED

1. A. I. Kiprianov, Usp. Khim., 40, 1283 (1971).
2. F. A. Mikhailenko, L. I. Shevchuk, and A. A. Shulezhko, Zh. Organ. Khim., 8, 1968 (1972).
3. F. A. Mikhailenko, A. N. Boguslavskaya, and A. I. Kiprianov, Khim. Geterotsikl. Soedin., 618 (1971).
4. W. West, S. Pearce, and F. Grum, J. Phys. Chem., 71, 1316 (1967).
5. F. A. Mikhailenko and A. N. Boguslavskaya, Khim. Geterotsikl. Soedin., 137 (1971).
6. U. Chiodoni and B. Mariani, Ann. Chim. (Roma), 53, 741 (1963).
7. A. I. Kiprianov and G. G. Dyadyusha, Ukr. Khim. Zh., 35, 609 (1969).
8. W. T. Simpson, J. Amer. Chem. Soc., 73, 5363 (1951).
9. V. I. Permogorov, G. G. Dyadyusha, F. A. Mikhailenko, and A. I. Kiprianov, Dokl. Akad. Nauk SSSR, 188, 1098 (1969).
10. V. I. Permogorov, Optika i Spektroskopiya, 34, 298 (1973).
11. G. G. Dyadyusha, Ukr. Khim. Zh., 30, 929 (1964).
12. G. Herzberg, Electronic Spectra and Structure of Polyatomic Molecules [Russian translation], Mir, Moscow (1969), p. 128.
13. S. G. Fridman and A. I. Kiprianov, Zh. Organ. Khim., 4, 696 (1968).
14. A. I. Kiprianov, I. L. Mushkalo, and F. A. Mikhailenko, Zh. Organ. Khim., 3, 2041 (1967).
15. A. I. Kiprianov, T. M. Verbovskii, and I. L. Mushkalo, Zh. Organ. Khim., 3, 2036 (1967).